FREE-RADICAL REACTIONS INVOLVING BISTRIFLUOROMETHYLAMINO-OXYL

BY

GREGORY D. CONNELLY, B.Sc.

This dissertation is submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy at the Victoria University of Manchester. Unless otherwise stated, the work described is that of the author and has not been submitted previously, in whole or in part, at this or any other University.

G. Campbell.

August, 1979.

The author graduated at Heriot-Watt University in July, 1975 with the degree of B.Sc.(Hons) in Chemistry, and between October, 1975 and October, 1978 was engaged in research work in the Chemistry Department at the University of Manchester Institute of Science and Technology (Faculty of Technology in the University of Manchester) under the direction of Professor R. N. Haszeldine F.R.S., and the supervision of Dr. A. E. Tipping.

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CONTENTS

SUMMARY

The initial purpose of this study was to investigate the reactions of bistrifluoromethylamino-oxyl with organic compounds with respect to free-radical rearrangements.

The reactions with 3,3,3-trichloropropene and 3,3,3-trichloro-2-methylpropene gave both rearranged and non-rearranged products with the yield of the former increasing, as expected, on dilution of the reactants.

With the chloroalkanes Me_2CClX (where X= Cl, Ph, or Me) overall elimination of hydrogen chloride was the major process, with the formation of bis(amino-oxy)-adducts from the resulting olefins.

The reaction of the oxyl with t-butyl bromide gave the non-rearranged compound $(CF_3)_2NOCH_2CMe_2Br$ together with products arising from β-scission of bromine.

With 2,2-diphenylpropane and t-butylbenzene complex mixtures were obtained, and only the non-rearranged products $(CF_3)_2NOCH_2CMePhX$ (where X= Ph and Me) were isolated.

The reaction of the oxyl with t-butyl acetate gave only non-rearranged products.

No evidence was obtained for rearrangement in the reaction of a 2:1 molar mixture of the oxyl and cyclopropylphenylmethane, although rearrangement possibly occurred to some extent with a 1:2 molar ratio of reactants in solution. With the cyclopropylcarbinols $\overline{CH_2CH_2CHCH(OH)X}$ (where X= Me and H), products arising from net oxidation were obtained in high yield, i.e. $\overline{CH_2CH_2CHCOY}$ [where Y= Me and $(CF_3)_2NO$].

Although no rearranged products were isolated from the reaction of the oxyl with 2-pinene, the compound

$(CF_3)_2NOCH_2\overline{C:CHCH_2CH[CMe_2ON(CF_3)_2]CH_2CH_2}$ was isolated in the reaction with 2(10)-pinene, indicating that ring opening of the cyclobutane ring had occurred.

Hydrogen abstraction was the major process in the reaction of the oxyl with allylbenzene and penta-1,4-diene; the formation of both the 1- and 3-substituted amino-oxy adducts indicated that an allylic radical was involved, rather than reaction by an addition-disproportionation mechanism. The 1-substituted isomers were further scavenged by the oxyl to give tris(amino-oxy)-substituted products.

The reaction of the oxyl with cyclo-octene and cis-cis-cyclo-octa-1,5-diene gave products resulting from hydrogen abstraction and addition; no evidence was obtained for rearrangement in either case.

The reaction with norbornadiene gave norborn-5-ene adducts, rearranged nortricyclanes, and tetra-substituted norbornanes, the relative yields of which varied with the concentration and relative ratios of the reactants.

The reaction of the oxyl with 2-phenylpropan-2-ol gave the compound $(CF_3)_2NOCH_2CPhMeON(CF_3)_2$ together with three isomeric dimers of α-methylstyrene. The NN-bistrifluoromethyl-hydroxylamine, formed in situ as a result of initial hydrogen abstraction by the oxyl, was shown to be a catalyst in the dehydration of the alcohol to α-methylstyrene.

The second part of this study involved the reactions of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane).

With the trichloropropenes $CH_2:CXCCl_3$ (where X= H and Me) the rearranged compounds $(CF_3)_2NCH_2CClXCCl_2ON(CF_3)_2$ were

obtained as major products; in the latter reaction the compound $(CF_3)_2NOCCl_2CMeClCH_2Cl$ was also formed presumably *via* chlorine atom attack on the alkene.

The reactions between the oxadiazapentane and *t*-butyl bromide and 2-chloro-2-phenylpropane were complex; the isolation of bromine and hydrogen chloride, respectively, indicated that β-scission of the halogen atom had occurred to some extent.

With 2-pinene, cyclopropylphenylmethane, and the cyclopropylcarbinols $\overline{CH_2CH_2CHCH(OH)X}$ (where X= H and Me) the reactions were complex indicating that ring-opening of the cyclobutyl and cyclopropyl rings had probably occurred.

The reaction with 2(10)-pinene gave a complex mixture of products including the compound $(CF_3)_2NCH_2\overline{C:CHCH_2CH[CHMe_2]CH_2CH_2}$ which is probably formed *via* hydrogen abstraction by the ring-opened intermediate radical from the starting olefin.

The reaction with cyclo-octa-1,5-diene gave products resulting from hydrogen abstraction and addition as well as the mono-substituted cyclo-octene $(CF_3)_2N\overline{CHCH_2CH_2CH_2CH:CHCH_2CH_2}$; no products arising from ring closure were isolated.

The oxadiazapentane was found to preferentially undergo addition to the double bond in allylbenzene and penta-1,4-diene, to give the products $(CF_3)_2NCH_2CHON(CF_3)_2CH_2X$ (where X= Ph and $-CH_2CH:CH_2$), rather than abstract an allylic hydrogen. In the liquid-phase reaction with penta-1,4-diene several very high-boiling products were also formed and it is postulated that these arise *via* reaction of the intermediate radicals with the diene.

The reaction between the oxadiazapentane and *t*-butyl-

benzene gave products arising from aromatic substitution and addition as the major products; the low yield of $(CF_3)_2NH$ isolated indicated that little hydrogen abstraction from the t-butyl group had occurred.

The reaction of the oxadiazapentane with chlorobenzene was also studied and although the products were not fully separated, it was apparent that both aromatic ring substitution and addition had occurred. Furthermore, the formation of hydrogen chloride indicated that some replacement of the ring halogen atom had taken place.

INTRODUCTION

Free-radical rearrangements.

A. Frequency of free-radical rearrangements.

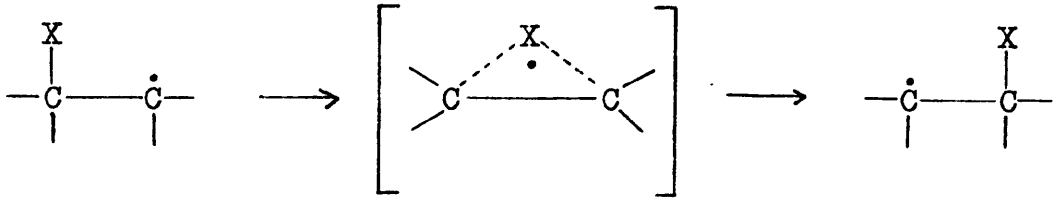
Under suitable conditions, free radicals may undergo intramolecular rearrangements, examples of which, although fairly numerous, are far less common than those involving carbenium ions. Particularly striking is the inability of alkyl groups to undergo 1,2-migration in radicals which compares with the extreme ease of such processes with the corresponding cations, e.g.

$$Me_3CCH_2\cdot \not\longrightarrow Me_2\dot{C}CH_2Me$$

$$Me_3CCH_2^+ \longrightarrow Me_2\overset{+}{C}CH_2Me$$

No rearrangements involving the 1,2-migration of hydrogen have been unambiguously shown to occur, although there are numerous examples of 1,2-shifts of aryl groups and halogen, together with instances of vinyl, acyl, and acetoxy group shifts.

Various treatments of L.C.A.O. molecular orbital calculations[1,2] have attempted to explain the more difficult nature of radical rearrangements compared to their cationic analogues with respect to 1,2-shifts, by considering that the rearrangement process occurs via a triangular arrangement, i.e.



Cationic rearrangements will bring the two electrons of the migrating group towards an empty orbital on the reactive centre, filling the bonding molecular orbital only. Radical and anionic rearrangements, however, have some antibonding character in the transition state as the orbital at the reactive centre is not empty. Consequently, it has been calculated that the triangular state is more stable than the linear one for the cation, hence facilitating rearrangement, but for the radical the stabilities of the two states are approximately the same, and for the anion the triangular state is less stable. Furthermore, the relative ease of migration in the radical with respect to 1,2-shifts is aryl > alkyl > hydrogen.

These theoretical treatments have been critisized[3], however, as they are based upon π approximations to what are essentially σ-electron systems in most cases.

An alternative mechanistic viewpoint has been proposed by Mayanz[4] based on the molecular vibrations of the radical. Basically, rearrangement is considered to be favoured when there is a high probability of an intramolecular vibration causing the appropriate geometry for migration. Heavier substituents, such as aryl or halogen, having low vibrational frequency modes, as well as increasing distance between the reaction site and migrating group were considered to be favourable structural features for rearrangement.

The energy differences between tertiary, secondary, and primary reaction centres appear to be far greater for cationic systems than for radical systems and as a result cationic

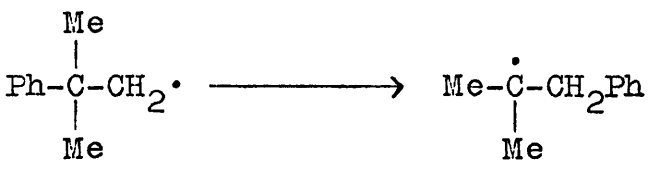
rearrangements are often subject to considerably greater driving forces and can be assisted by a suitable choice of solvent.

Further, cationic rearrangements can be simultaneous (or to some degree concerted) with development of charge. Radical rearrangements, however, appear to involve discrete rearranged and non-rearranged radicals, and although several authors have proposed that β-halogenoalkyl substituents can anchimerically assist vicinal hydrogen abstraction *via* a bridged halogen structure, such examples of neighbouring-group participation are far less common in radical chemistry. Consequently, the radical-rearrangement step is in competition with other side reactions, and as a result the number and types of radical rearrangement are reduced.

B. 1,x-Shifts

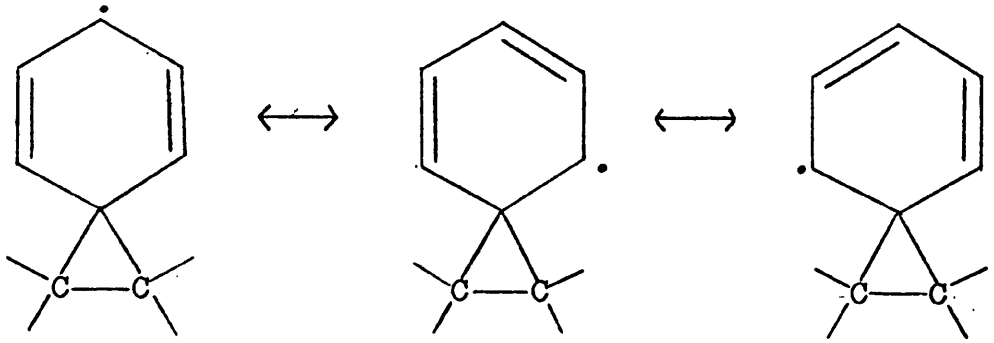
(i) Aryl shifts.

The 1,2-shift of the phenyl group, commonly known as the 'neophyl' rearrangement, was first discovered in a Kharasch-Grignard reaction in 1944[5]; the driving force for the migration is the formation of a tertiary radical from a primary radical, *i.e.*



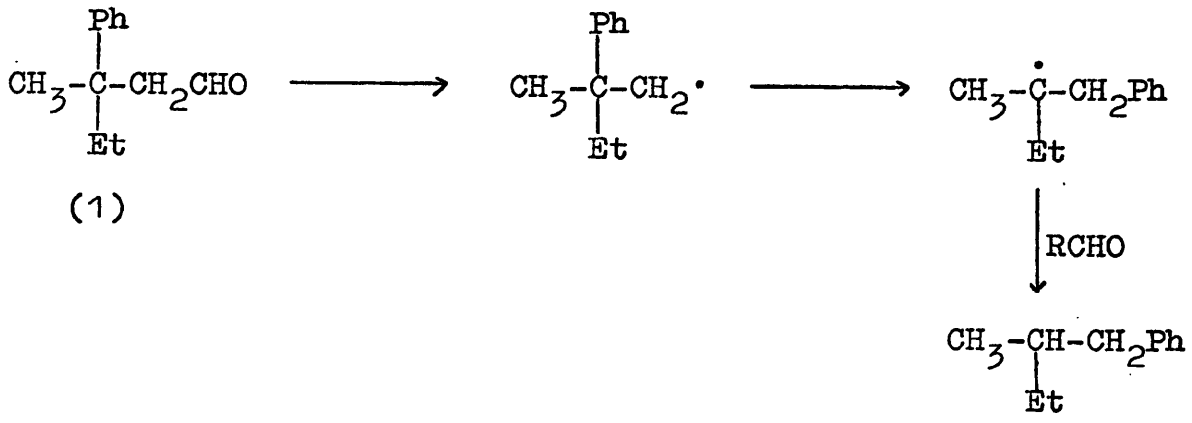
The rearrangement step is believed to proceed through a triangular transition state with the odd electron delocalised

round the aromatic ring, i.e.



The question arises as to whether the bridged structure exists as a distinct intermediate or is involved only as a transition state, hence involving discrete rearranged and non-rearranged radicals. A study of the e.s.r. spectrum of the 2-phenylethyl radical[6] failed to indicate any evidence of the bridged intermediate, and work showing that the extent of rearrangement is inversely dependent on substrate concentration[7,8,9] and is decreased if efficient chain-transfer agents are present[10,11,12] tends to support the idea that rearrangement involves discrete rearranged and non-rearranged radicals.

If a bridged radical is involved as a discrete intermediate one would expect to observe both evidence of anchimeric assistance and control of stereochemistry. However, evidence of rate enhancement by neighbouring-group participation was not found in a study of the relative rates of decomposition of the compounds $\left[PhCMe_2CH_2CO_2\right]_2$,[13] $\left[PhCH_2CH_2CO_2\right]_2$, and $\left[PhCH_2CH_2CH_2CO_2\right]_2$[14] and Ruchardt has shown that the decarbonylation of the optically-active aldehyde (1) gives 98% racemic product, i.e.



Although the above evidence tends not to support the existence of a bridged intermediate it does not exclude the possibility of the formation of a bridged transition state, or indeed a number of these transition states, in the rearrangement step.

The extent of rearrangement of β-arylalkyl radicals is markedly dependent on the lifetime of the radical as well as on the activation energy for the rearrangement process. The lifetime of the radical is dependent on the intrinsic stability of the non-rearranged radical, and also on the ease with which it undergoes chain transfer. The stability of the rearranged radical plays an important part in determining the activation energy for the rearrangement process.

The importance of the relative stabilities of the rearranged and non-rearranged radicals, and to a lesser extent the steric congestion at the β-carbon, on the extent of rearrangement is shown in Table 1.

TABLE 1

Extent of rearrangement of β-phenylalkyl radicals.

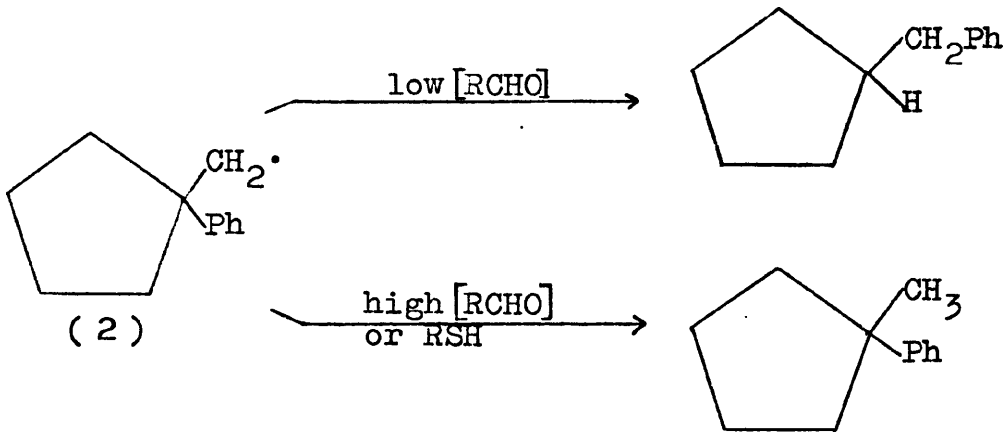
Initial radical	Rearranged radical	Extent of rearrangement (%)	Reference
$Ph_3CCH_2\cdot$	$Ph_2\dot{C}CH_2Ph$	100	15
$Ph_2CMeCH_2\cdot$	$Ph\dot{C}MeCH_2Ph$	100	16
$Ph_2CHCH_2\cdot$	$Ph\dot{C}HCH_2Ph$	63	15
$PhCMe_2CH_2\cdot$	$Me_2\dot{C}CH_2Ph$	49	15
$PhCHMeCH_2\cdot$	$Me\dot{C}HCH_2Ph$	39	15
$PhCH_2CMe_2\cdot$	$\dot{C}H_2CMe_2Ph$	0	17

An increase in radical stability is not intrinsically necessary for rearrangement, however, particularly if elevated temperatures are used which favour the rearrangement step. For example, labelling experiments have shown that the β-phenylethyl radical itself rearranges with the extent of rearrangement varying from 2% at 145 °C to 5% at 175 °C,[16] i.e.

$$PhCH_2-{}^{14}CH_2\cdot \longrightarrow \dot{C}H_2-{}^{14}CH_2Ph$$

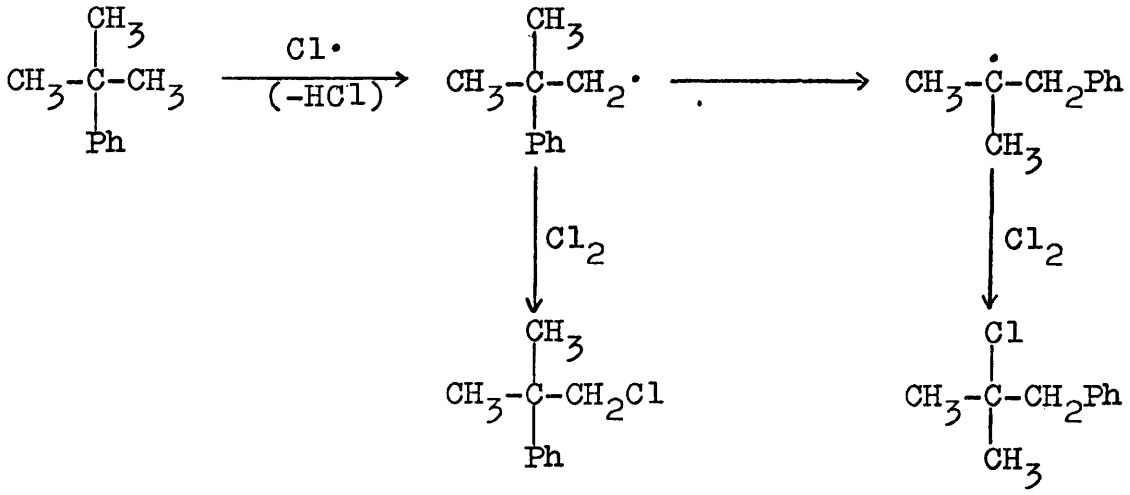
The extent of rearrangement is also dependent on the nature and concentration of chain-transfer agent in the reaction environment. For example, Wilt and Philip[11] found that the rearrangement of radical (2) increased from 63% to 92% as the concentration of aldehyde was decreased, while on addition of benzyl mercaptan (a good chain-transfer agent)

rearrangement decreased to less than 3%, i.e.



(2)

It is for this reason that aryl migrations are not commonly observed in free-radical halogenations, although at higher temperatures some rearrangement has been observed[18] i.e.



(major) (minor)

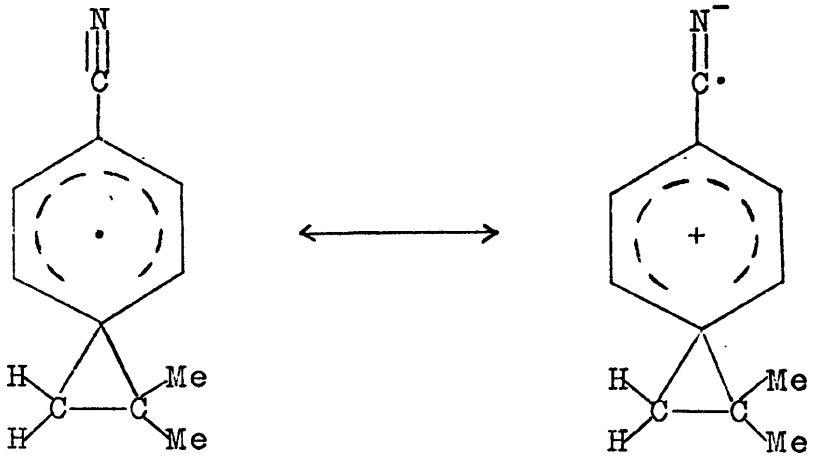
Ruchardt[19] has shown that the extent of rearrangement is dependent on the nature of the migrating aryl group. His results seem to indicate that electron-withdrawing substituents favour rearrangement (Table 2).

TABLE 2

Relative amounts of aryl migration (%) in $ArCMe_2CH_2^{\bullet}$ radicals

Substituent in aryl group	Yield of rearranged product (%)
p-MeO	0.36
H	1.00
p-Cl	1.76
p-NO_2	31
p-CN	35

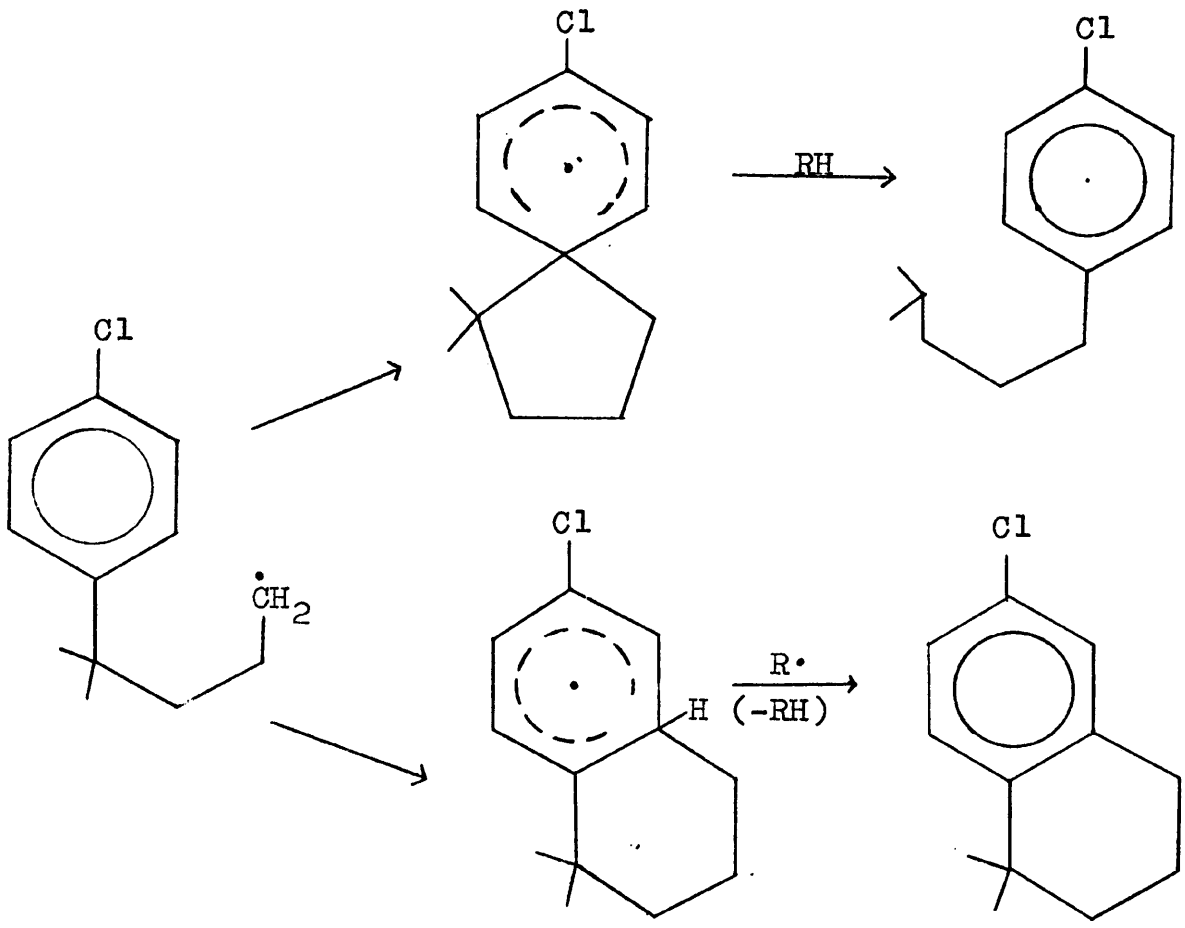
A possible explanation is the ability of electron-withdrawing groups to impart some carbenium ion character to the transition state, hence increasing its stability, i.e.



There is little evidence for homolytic 1,3-phenyl migration and it is believed that the unfavourable four-membered transition state which would be involved precludes the rearrangement.

However, examples of both 1,4- and 1,5-phenyl migrations have been recorded. The evidence available indicates that the rearrangements proceed through bridged transition states, involving discrete rearranged and non-rearranged radicals rather than *via* distinct intermediates, although it would be expected that involvement of five- or six-membered ring intermediates would be more favourable than involvement of three-membered ring intermediates in 1,2-shifts.

The rearrangement step involved in 1,4-aryl shifts may proceed *via* either five- or six-membered transition states (or intermediates) or both, *e.g.*[20]



Aryl shifts from carbon to oxygen and from oxygen to oxygen are also known[21], and a 1,2-shift of phenyl from oxygen to carbon has been reported at high temperature[22], i.e.

$$PhOCH_2\cdot \longrightarrow PhCH_2O\cdot$$

Both 1,4- and 1,5-phenyl shifts from silicon to carbon have been shown to occur[23], e.g.

$$Me_2\overset{Ph}{\overset{|}{Si}}CH_2CH_2CH_2\cdot \longrightarrow Me_2\dot{S}iCH_2CH_2CH_2Ph$$

$$Me_2\overset{Ph}{\overset{|}{Si}}CH_2CH_2CH_2CH_2\cdot \longrightarrow Me_2\dot{S}iCH_2CH_2CH_2CH_2Ph$$

and shifts from silicon[24] and germanium[25] to oxygen have been reported.

However, no evidence for a 1,2-aryl shift from silicon to carbon has been found[26,27], i.e.

$$Ph_3SiCH_2\cdot \not\longrightarrow Ph_2\dot{S}iCH_2Ph$$

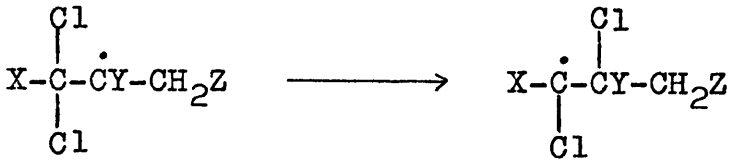
It has been suggested that the carbon radical is stabilised by interaction of the unpaired electron with the d-orbitals of silicon and that the degree of steric crowding round the silicon atom is less than that around carbon in the radical $Ph_3CCH_2\cdot$ which reduces the driving force for rearrangement. Furthermore, it has been postulated that the transition state for rearrangement would be subject to considerable strain compared to its carbon analogue. These factors are apparently less important in the case of 1,4- or 1,5-phenyl shifts from silicon to carbon.

(ii) Halogen shifts.

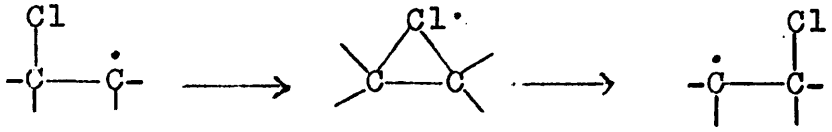
The 1,2-shift of chlorine, known as the Nesmeyanov rearrangement, is the most common in this class of rearrangement. The first authenticated report, which appeared in 1951[28] was based on the observation that the peroxide- or light-catalysed addition of hydrogen bromide to 3,3,3-trichloropropene led to rearranged products, i.e.

$$CH_2{:}CHCCl_3 \xrightarrow{HBr} BrCH_2CHClCHCl_2$$

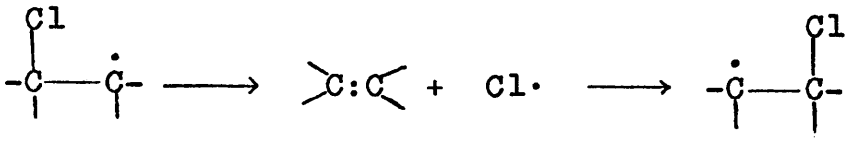
Subsequent work has provided many examples of vicinal chlorine shifts, mainly centred around processes of the type shown below[29] (where X= H, F, Cl, or CH_3; Y= H, Cl, Br, or CH_3; Z= H, Br, CCl_3, or SR)



The rearrangement is believed to proceed through a bridged radical intermediate (or transition state) in which the extra electron is accommodated in a d-orbital on chlorine, i.e.



An alternative mechanism by which the rearrangement step may occur is via an intermolecular elimination-readdition pathway, i.e.



Such a process is possibly more important at higher temperature when the β-scission of chlorine is favoured, and indeed it has been suggested that all halogen rearrangements occur via an elimination-readdition process[31].

As with 1,2-aryl shifts, the most important factor governing the extent of 1,2-halogen migration is the relative stabilities of the rearranged and non-rearranged radicals and consequently the relative rates of their interaction with the chain-transfer agent. The extent of migration in several β-chloroalkyl radicals are shown in Table 3.

TABLE 3

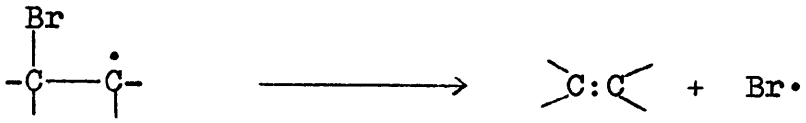
Benzoyl peroxide initiated reaction of HBr with various chloro-olefins

Initial radical	Rearranged radical	Yield (%)	Reference
$Cl_3\dot{C}HCH_2Br$	$Cl_2\dot{C}CHClCH_2Br$	77	28
$Cl_2CH\dot{C}HCH_2Br$	$Cl\dot{C}HCHClCH_2Br$	46	32
$CHCl_2\dot{C}ClCH_2Br$	$Cl\dot{C}HCCl_2CH_2Br$	0	32

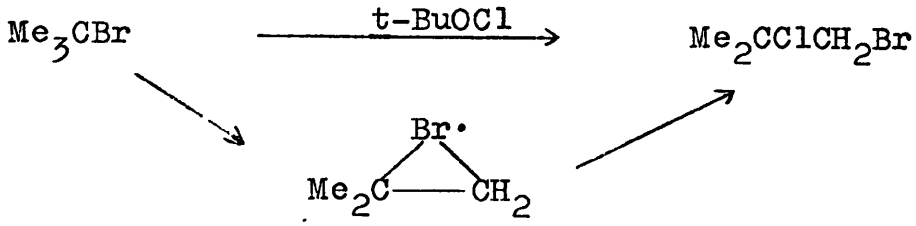
Also, as the energy of activation of the chain-transfer step is decreased, the ratio of non-rearranged to rearranged product is increased. Thus, in a study of free-radical additions to 3,3,3-trichloropropene at 80 °C[29] it was observed that the yield of rearranged 1:1 alduct decreased when the

addend was changed from molecular bromine to thiophenol in agreement with the known greater efficiency of the latter addend as a chain-transfer agent.

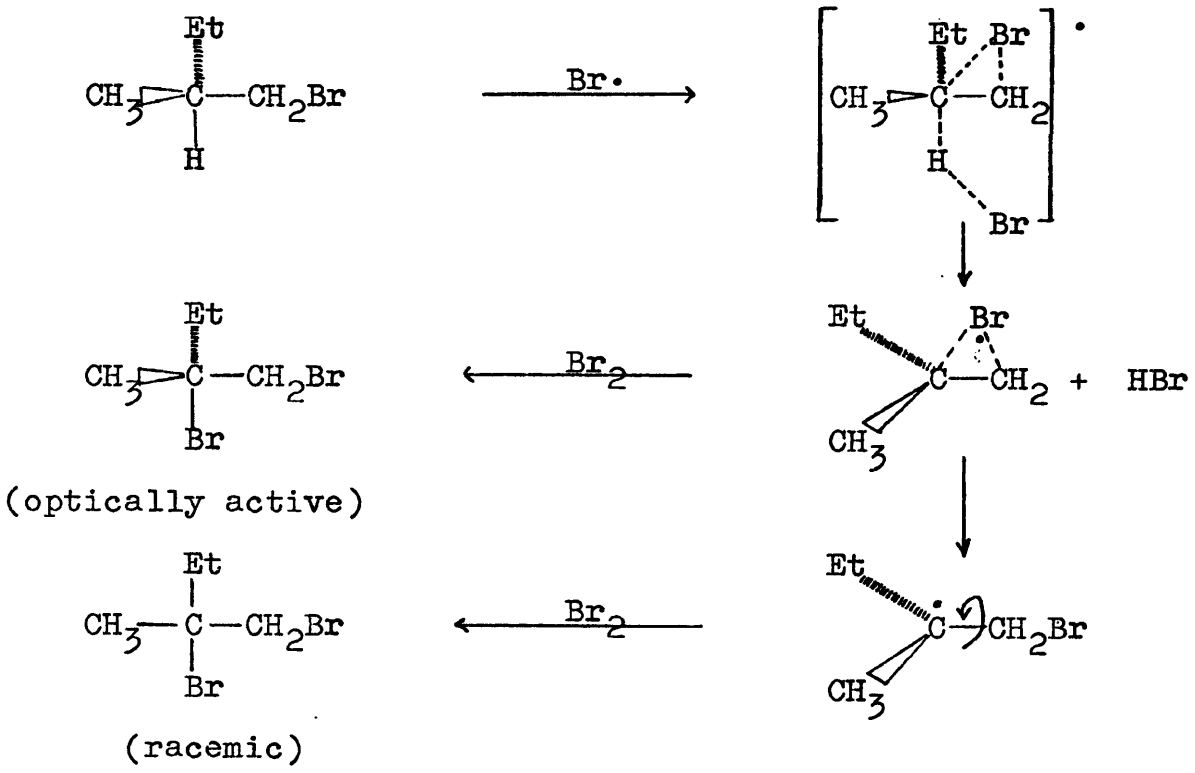
The mechanism of similar 1,2-shifts of bromine has been in dispute because the rearrangement step would be expected to be in competition with the relatively facile elimination of the β-bromine substituent to form unsaturated products, i.e.



However, Skell et. al.[33] and others[34,35] have claimed that such vicinal bromine shifts do occur via a non-classical bridging bromine atom, e.g.



The evidence cited in favour of bridged halogen intermediates (or transition states) has been based on several grounds[36]. For example, the free-radical bromination of (+)-1-bromo-2-methylbutane yielded as a single product 1,2-dibromo-2-methylbutane, of high optical purity, indicating the intermediacy of a bridged species, which can isomerise to the classical radical[37], i.e.



The photobromination of the corresponding chloride also gave optically active product, but a much greater bromine concentration was required for retention of stereochemistry.

Notably, with less reactive trapping agents, e.g. Cl_2 or t-BuOCl, the optically active halides gave racemic products[37,38] which also indicates a limited lifetime for the bridged halogen radicals, before isomerisation to the classical radicals occur.

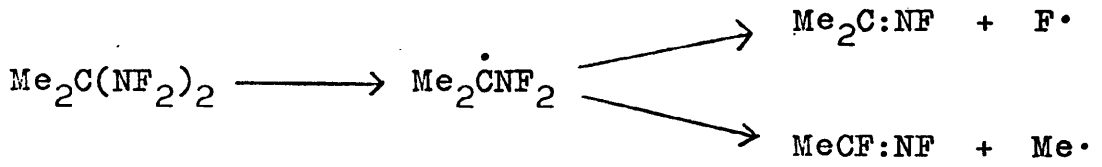
However, such evidence of steric control has been criticized[39] on the basis that although a β-cyano group would not be expected to be able to serve as a bridging group, it was found that bromination of optically active 3-methylvaleronitrile gave optically active 3-bromo-3-methylvaleronitrile, indicating that a bridged structure is not necessary for retention of optical activity. Similarly, the selectivity

observed under suitable conditions for abstraction of a hydrogen β- to a bromine atom, which has been attributed to anchimeric assistance and the formation of a bridged radical intermediate,[34,40,41] or a less symmetrical structure involving weak interactions between the C-halogen bond and the radical p-orbital[42], may be explained by alternative mechanistic pathways[43].

Although the mechanism of 1,2-halogen shifts is still in doubt, it appears that if a non-classical bridged radical intermediate is involved, it is best favoured by the heavier elements, there being no evidence for bridging involving first-row elements.

Under suitable conditions, for example when the β-hydrogen abstraction step is an endothermic process and an antiperiplanar configuration may be assumed, the development of bridging may be simultaneous with development of radical character. Once formed, the bridged radical may isomerise to a classical radical, either before or after the rearrangement step, or may exist until chain-transfer occurs, with the direction of opening being governed by the relative stabilities of the rearranged and non-rearranged radicals.

Although the interpretation of the mechanism of vicinal halogen migration involving an expanded valence shell would preclude the occurrence of a 1,2-fluorine migration, as fluorine could not accomodate the extra electron, there has been one report of an apparent 1,2-shift of fluorine[44], i.e.



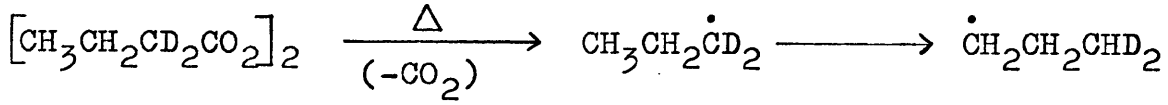
The authors discounted the possibility of an elimination-addition mechanism by claiming that hydrogen abstraction would occur preferentially with respect to addition, and that the driving force for the rearrangement stems from the exothermicity[45] of the reaction.

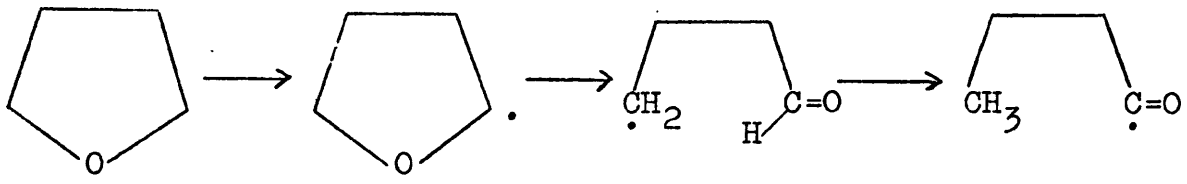
(iii) Hydrogen shifts

In contrast to the ease of rearrangement of hydrogen via 1,2-shifts in cationic chemistry, there are no authenticated examples of 1,2-hydrogen migrations in radicals.

The triangular transition state for the vicinal migration of a hydrogen atom would allow considerably less delocalisation of the unpaired electron than is the case for phenyl or halogen shifts, and would be therefore much less favourable[1,2]. Furthermore, the migration of the light element hydrogen is considered to lower the probability of a properly orientated vibrational mode for rearrangement.[4]

Both 1,3- and 1,4-hydrogen migrations have been reported,[46,47] e.g.



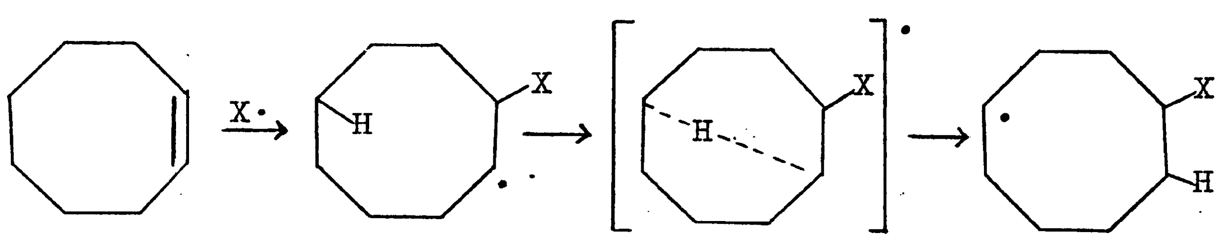


However, examples of such shifts are relatively rare and rearrangement has not been observed in certain cases where it would be expected, e.g.[48]

$$Me_2CHCH_2\dot{C}H_2 \not\longrightarrow Me_2\dot{C}CH_2CH_3$$

Reutov[49] has suggested that 1,3-hydrogen migration only occurs when the transition state for rearrangement has a high degree of symmetry although the factors affecting 1,3- and 1,4-hydrogen migrations are still in considerable doubt.

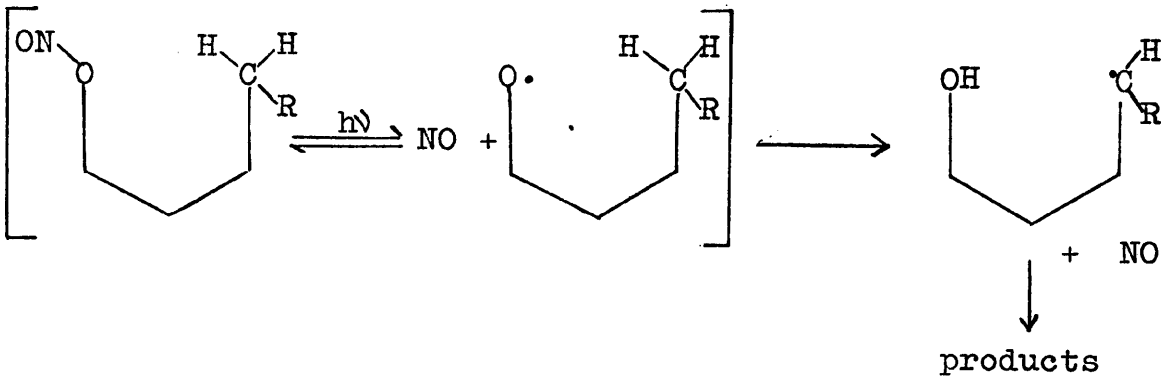
In contrast to the small number of examples of 1,3- and 1,4-hydrogen migrations, there are numerous examples of 1,5-hydrogen shifts. One explanation that has been proposed is that intramolecular hydrogen transfer requires that the attacking centre and the bond under attack approach colinearity as in radical displacement reactions.[50] With 1,5-hydrogen migrations a distorted six-membered ring transition state becomes possible which allows an approach to colinearity among the three atoms involved in the transfer step, e.g.[51]



Although hydrogen migrations involving larger ring transition states (e.g. 1,6-shifts) should allow even more colinearity in the transition state, the probability that the preferred conformers for such shifts would exist long enough for them to occur decreases with increasing chain length.

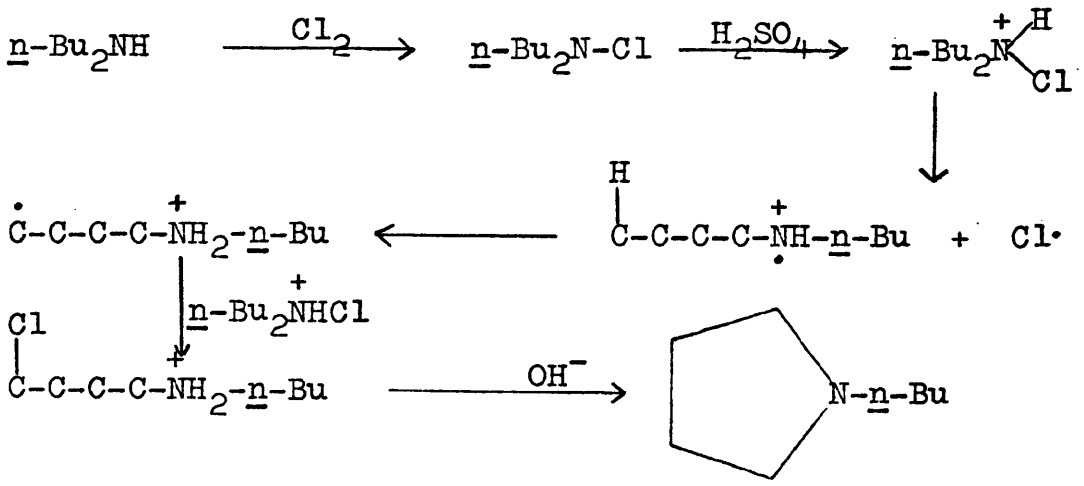
As expected, the extent of hydrogen migration in a given system is markedly dependent on the nature and concentration of chain-transfer agent. For example, it was found that in radical addition to cyclo-octene the yield of rearranged product decreased on changing the addend from carbon tetrachloride to trichloromethanesulphonyl chloride to bromotrichloromethane[51] which parallels the increasing efficiency of the addends as chain-transfer agents.

There are numerous examples of 1,5-hydrogen migrations from carbon to oxygen in the literature. The best example is perhaps the well known Barton reaction, e.g.[52]



The driving force for 1,5-hydrogen migration from carbon to oxygen is greater than that for the analogous shift to carbon as the new O-H bond is stronger than the C-H bond which is broken. As in carbon to carbon hydrogen migrations, 1,5-shifts are the most common although in some cases 1,6-hydrogen migration may compete with the 1,5-hydrogen shift.[53,54]

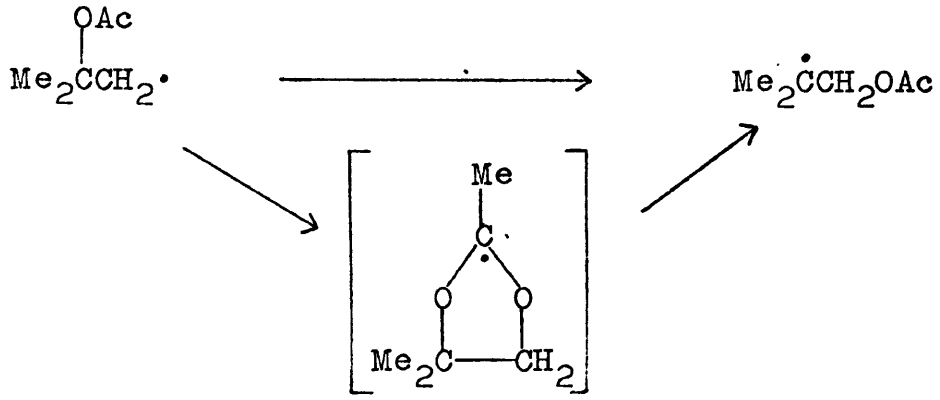
The Hofmann-Loffler-Freytag reaction[55] involves the homolytic migration of hydrogen from carbon to nitrogen. Once again, 1,5-hydrogen migration is generally favoured, e.g.[56]



although in certain cases 1,6-hydrogen transfer may become important[57].

(iv) Acyloxy shifts

Acetoxy groups may undergo homolytic 1,2-shifts, e.g.

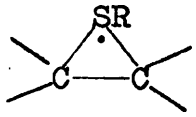


The driving force for the rearrangement is the formation of a tertiary radical from a primary radical. The mechanism of the rearrangement step is believed to occur via a five-membered intermediate (or transition state) rather than by an elimination-addition pathway as added isobutylene was without effect in the process.

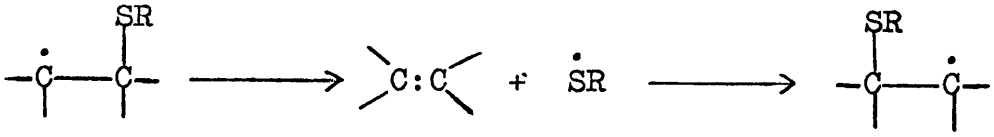
Interestingly, a corresponding 1,3-acetoxy shift (which would involve a six-membered ring species) was not observed in cases where it might have been expected[58,59].

(v) Alkylthiyl- and arylthiyl-shifts

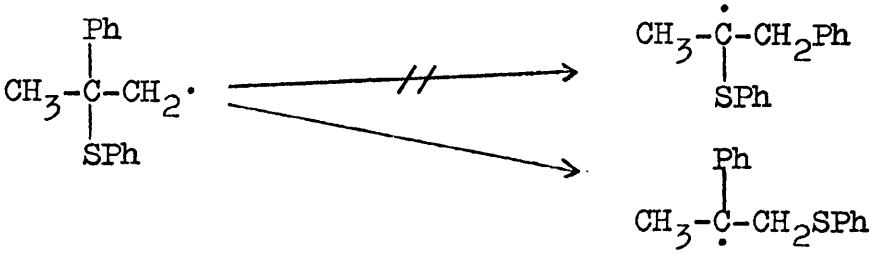
Thiols can undergo rearrangement under suitable free-radical conditions. As in halogen migrations, a bridged transition state (or intermediate) in which sulphur has undergone octet expansion to accommodate the extra electron, is probably involved, i.e.



However β-thioalkyl radicals readily undergo β-scission, particularly at elevated temperatures,[62] and the rearrangement may conceivably occur via an elimination-addition process, i.e.



Under conditions where a 1,2-phenyl shift is in competition with a 1,2-thiophenyl shift, the latter group has been shown to migrate preferentially,[63] e.g.



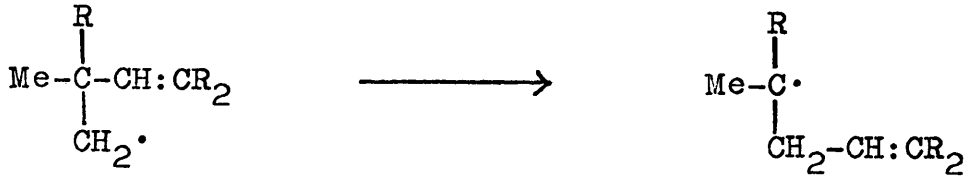
This has been attributed to the fact that sulphur can expand its octet, whereas the three-membered ring species involved in a 1,2-aryl shift involves loss of aromaticity of the aryl group.

However, the situation is not so simple as this since

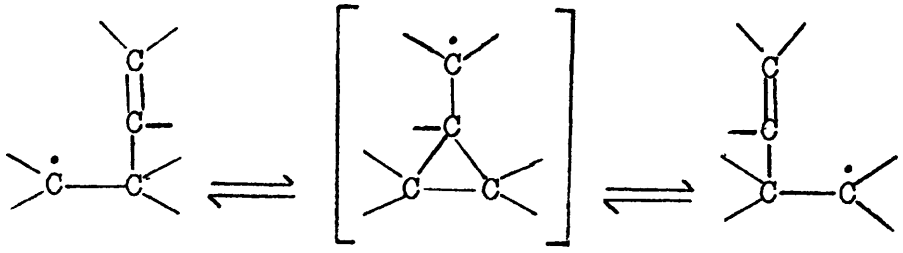
even if the rearrangement occurs purely *via* an intramolecular mechanism, the radical resulting from rearrangement of the thiophenyl group cannot be expected to have the same stability as that resulting from a 1,2-phenyl shift.

(vi) *Vinyl shifts*

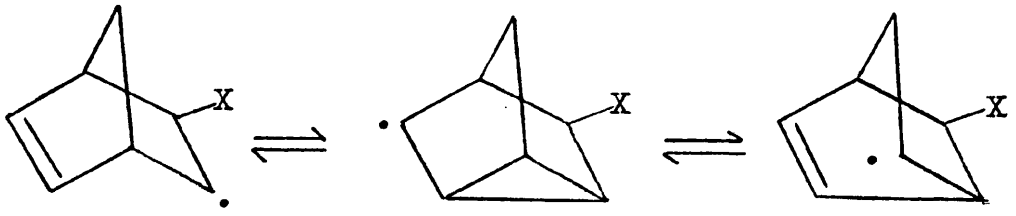
Vinyl groups have been reported to rearrange *via* 1,2-shifts, *e.g.*[64]



The migration is considered to proceed *via* a bridged intermediate cyclopropylcarbinyl radical, *i.e.*



Consecutive cyclisation and fragmentation frequently leads to net migration of vinyl groups in substituted homoallylic radicals, particularly when the structural features favour rearrangement,[3,21] *e.g.*

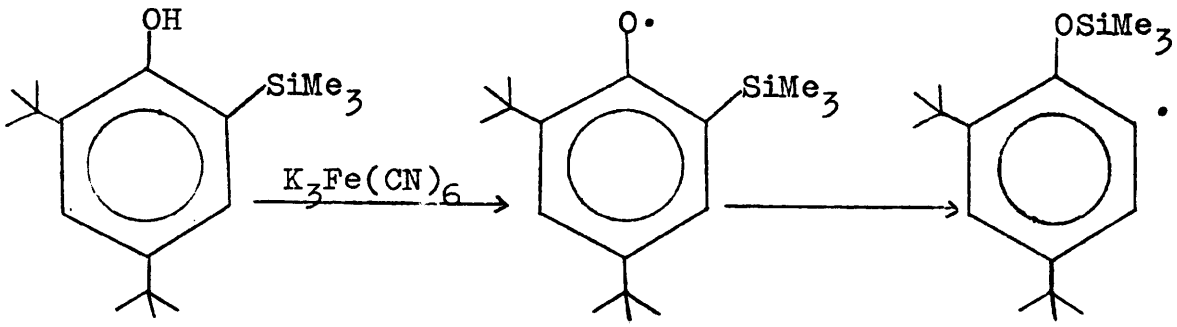


(vii) Trialkylsilyl shifts

The vicinal migration of the trimethylsilyl group has been reported[65] to occur at high temperature, i.e.

$$Me_3SiSiMe_2CH_2\cdot \xrightarrow{600\ ^{\circ}C} \dot{S}iMe_2CH_2SiMe_3$$

An unprecedented 1,3-shift of the trimethylsilyl group has been claimed in the oxidation of compound (3)[66], i.e.

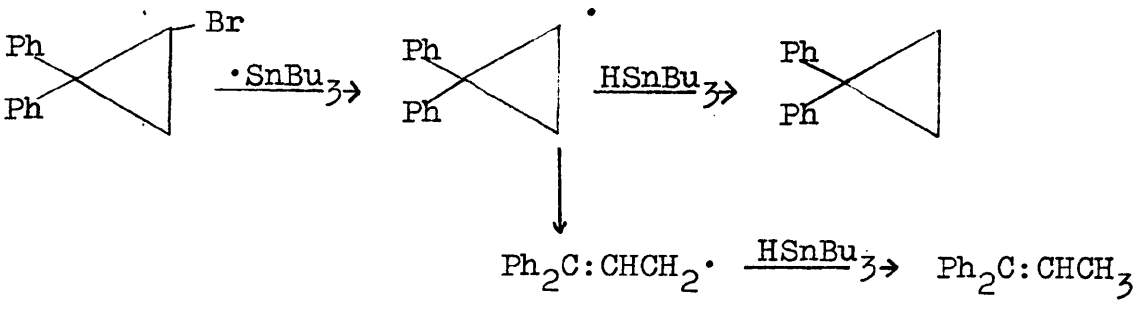


(3)

The formation of the strong Si-O bond is probably the driving force for this rearrangement.

C. Intramolecular fragmentations

Cyclopropyl radicals do not generally undergo ring opening even though relief of ring strain and the formation of an allylic radical would result. Ring opening has been observed, however, with certain substituted cyclopropyl radicals which give rearranged radicals which are resonance stabilised, e.g.[67]



As expected, the yield of ring-opened acyclic product increased on dilution of the reactants and on increasing the reaction temperature.

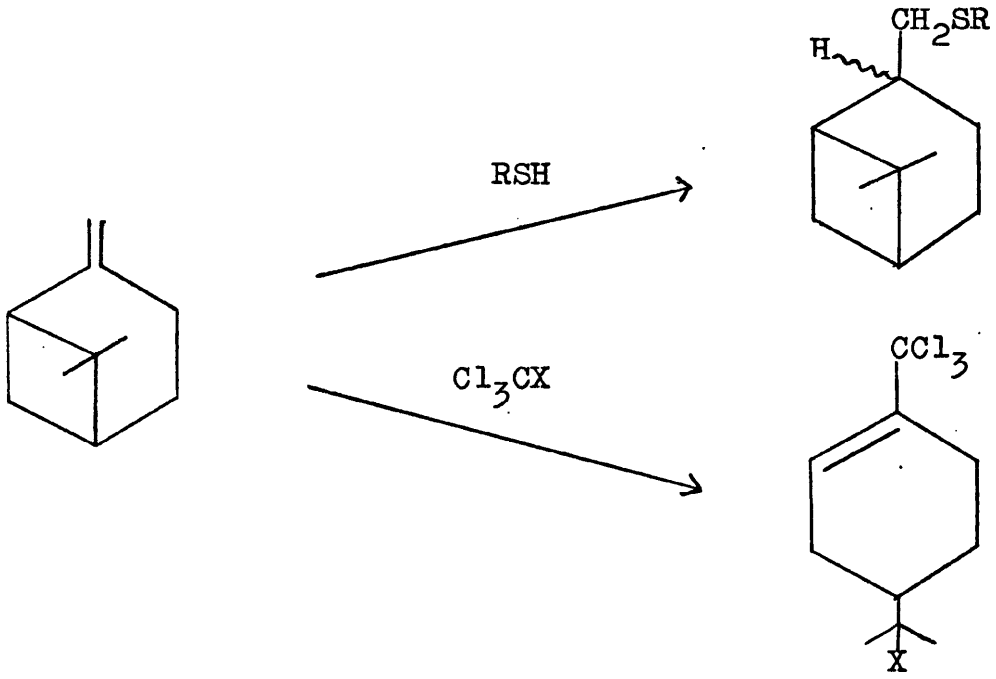
In contrast, cyclopropylmethyl radicals readily rearrange *via* ring opening to give homoallyl radicals, *i.e.*

The homoallyl radicals may themselves rearrange *via* cyclopropylcarbinyl radical intermediates, leading to the net migration of a vinyl group (p. 21).

The driving force for the rearrangement is the relief of ring strain in the cyclopropyl ring, and the equilibrium between the cyclic and ring-opened radicals generally favours the acyclic species, except in cases where the cyclised radical is particularly stabilised. Significant yields of non-rearranged products may be obtained, however, by the addition of efficient chain-transfer agents, such as thiols.[21]

The fragmentation of cyclobutyl radicals is very much less facile than that of cyclopropylmethyl radicals and the energy of activation for such fragmentation is reported to be *ca.* 75 kJ/mol.[68]

Cyclobutylcarbinyl radicals, however, have been shown to undergo intramolecular fragmentation under suitable conditions, *e.g.*[69] (where X= Br,or Cl)

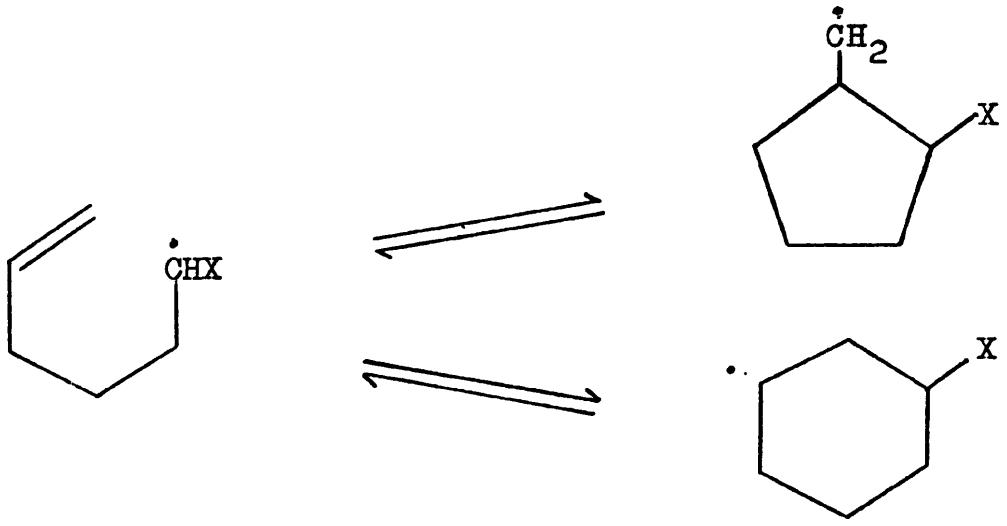


Once again the driving force for the rearrangement is believed to be the relief of angular strain in the cyclobutane ring which accompanies the rearrangement, and the formation of a tertiary radical from a secondary radical. As expected, the extent of rearrangement is dependent on the temperature[70], and with an efficient chain-transfer agent, such as thiolacetic acid, only non-rearranged products are obtained.[69]

D. Cyclisation

The cyclisation of hex-5-en-1-yl and related radicals to form five- and six-membered ring radicals has been the subject of considerable research. In cases where closure to both five- and six-membered ring radicals can occur, the kinetic preference is for the former, while the thermodynamic preference is for the latter. When the acyclic radical is stabilised, the cyclisation becomes reversible[71] and the

proportion of stabler six-membered ring species increases, i.e. (where X= H, Ph, or CO_2Et)



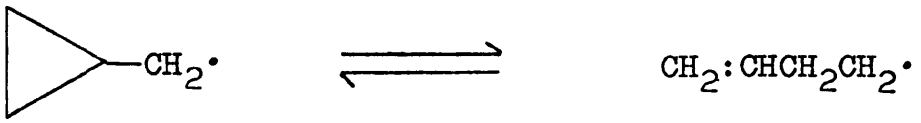
The effect of the substituent (X) on the ratio of five- and six-membered ring products is shown in Table 4.[71]

TABLE 4

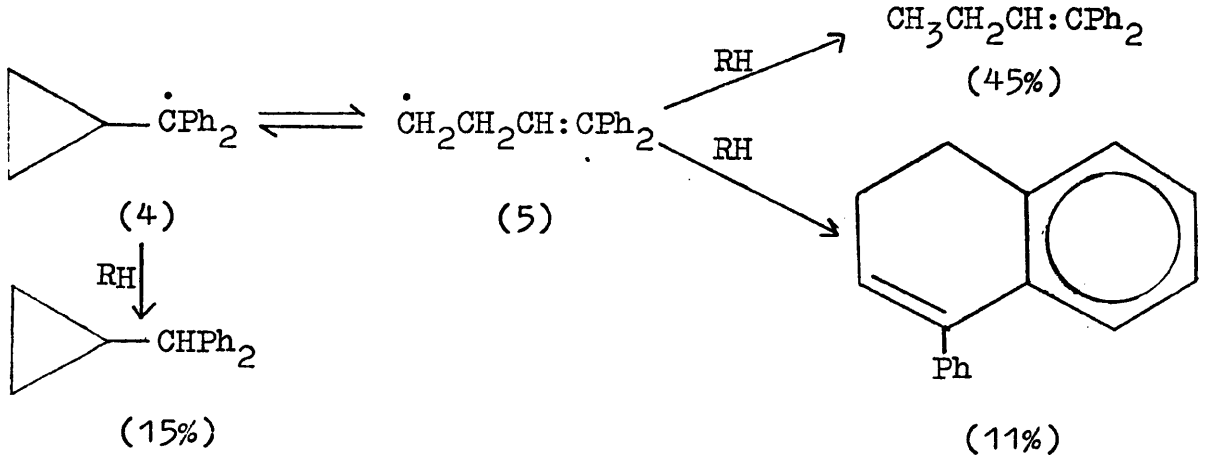
Relative amounts of five- and six-membered products in the cyclisation of $CH_2{:}CHCH_2CH_2CH_2\dot{C}HX$

Substituent (X)	Five-membered product (%)	Six-membered product (%)	Reference
H	100	0	72
Ph	92	8	73
CO_2Et	56	44	74

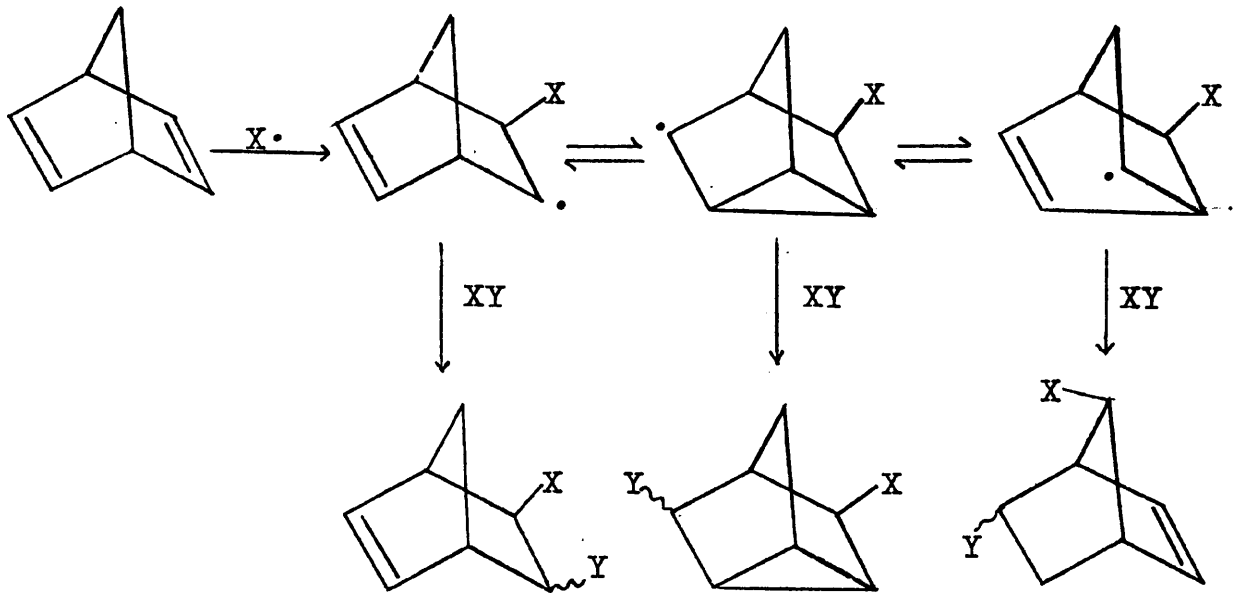
The cyclisations of but-3-en-1-yl (homoallyl) and pent-4-en-1-yl radicals have been studied in less detail. Homoallyl radicals are formed reversibly by fragmentation of cyclopropylmethyl radicals, i.e.



In most cases the equilibrium lies far to the right, although products containing the cyclopropyl ring may be formed in the presence of an efficient chain-transfer agent. When the cyclised and ring-opened radicals are highly stabilised, as in radicals (4) and (5), the energy barrier between the two species is reduced and both ring-opened and cyclic products are obtained[75], i.e. (where RH= cyclohexa-1,4-diene)



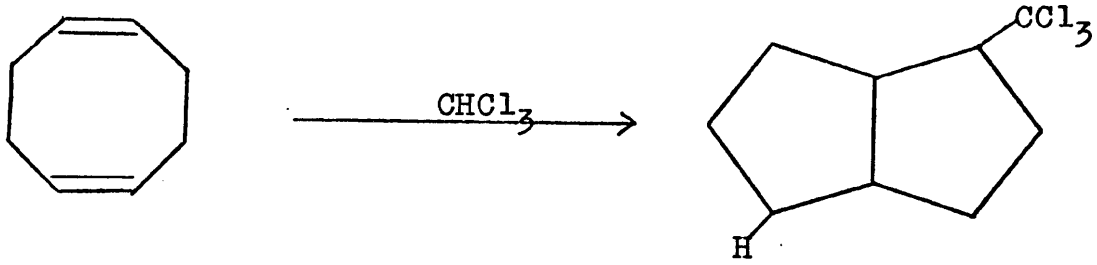
Cyclisation may occur with radicals in which the stereochemistry favours such reaction, as is found with various radical additions to norbornadiene, i.e.



The extent of rearrangement depends on whether the equilibrium can be established in the reaction environment, and as expected, the yield of rearranged nortricyclane product is reduced in the presence of efficient chain-transfer agents such as thiols.

No instances are known in which a homoallyl radical cyclises to a cyclobutyl radical, although such rearrangement would result in the formation of a secondary radical, and it is therefore considered that the transition state for such a process is particularly unfavourable.

The cyclisation of pent-4-en-1-yl radicals is apparently less favourable than that of hex-5-en-1-yl radicals and significant yields of cyclised products are only obtained when the molecule contains structural or electronic features which could favour the cyclisation process. An interesting example of a molecule in which the structure particularly favours cyclisation is cyclo-octa-1,5-diene, radical addition to which results in the formation of bicyclic products,[76] i.e.

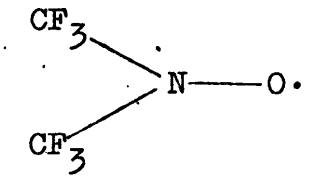


(37%)

No instances have been reported in which pent-4-en-1-yl radicals cyclise to cyclobutylmethyl radicals.

Bistrifluoromethylamino-oxyl

The oxyl (6), first reported by Haszeldine[77], Makarov and co-workers[78], and Blackley and Reinhard[79], exists as a stable free radical at room temperature and has the structure (6).



(6)

It is a purple gas (b.p. -20 °C) which on cooling condenses to a brown liquid and finally to a yellow solid (m.p. ca. -70 °C), and may be prepared by the oxidation of NN-bistrifluoromethylhydroxylamine using a variety of oxidising agents including fluorine, silver(1) oxide, potassium permanganate, and cerium(1V) sulphate.

In common with other nitroxyls which do not contain any α-hydrogen atoms, the oxyl does not undergo disproportionation even at temperatures up to 200 °C, but the compound decomposes to a large extent at 350 °C[80].

Extensive work in this department[81] has shown that the oxyl (6) reacts with olefins to form 2:1 adducts, e.g.

$$(CF_3)_2NO\cdot + CH_2{:}CH_2 \longrightarrow (CF_3)_2NOCH_2CH_2\cdot$$

$$(CF_3)_2NOCH_2CH_2\cdot + (CF_3)_2NO\cdot \longrightarrow (CF_3)_2NOCH_2CH_2ON(CF_3)_2$$

It was also found that the oxyl (6) reacts faster with tetrafluoroethylene than with ethylene and it was initially believed that this indicated that the oxyl has nucleophilic character. However, subsequent work on the relative rates of reaction of the oxyl with a series of olefins has shown that the oxyl reacts faster with electron-rich olefins and that the result with tetrafluoroethylene was atypical.[82] It is therefore now believed that the oxyl has electrophilic character.

The oxyl reacts with organic substrates by abstraction of hydrogen followed by scavenging of the resultant radicals, e.g.

$$(CF_3)_2NO\cdot + PhCH_3 \longrightarrow (CF_3)_2NOH + PhCH_2\cdot$$

$$PhCH_2\cdot + (CF_3)_2NO\cdot \longrightarrow (CF_3)_2NOCH_2Ph$$

As expected, the ease of hydrogen abstraction decreases in the order tertiary > secondary > primary.

A study of the reaction of the oxyl with alkanes[82] showed that 1,2-disubstitution products were formed as well as the expected monosubstitution product, particularly with branched alkanes, e.g.

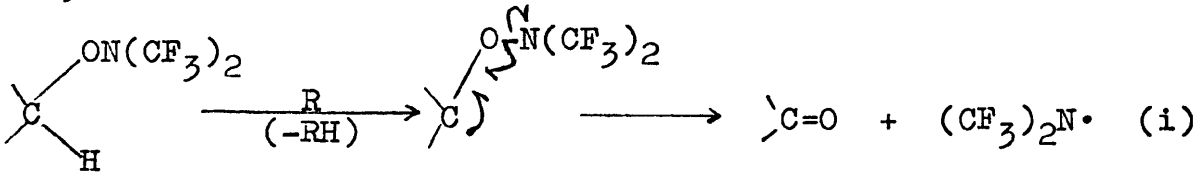
$$Me_3CH + 4(CF_3)_2NO\cdot \longrightarrow (CF_3)_2NOCMe_2CH_2ON(CF_3)_2 + 2(CF_3)_2NOH$$

When the reaction was carried out in carbon tetrachloride solution[83] it was found that the yield of disubstitution product increased at the expense of the monosubstitution product. Evidence was obtained which showed that this reaction involved hydrogen abstraction by the oxyl to afford the alkene, $Me_2C{:}CH_2$, which then underwent addition by the oxyl to give the observed 1,2-disubstitution product.

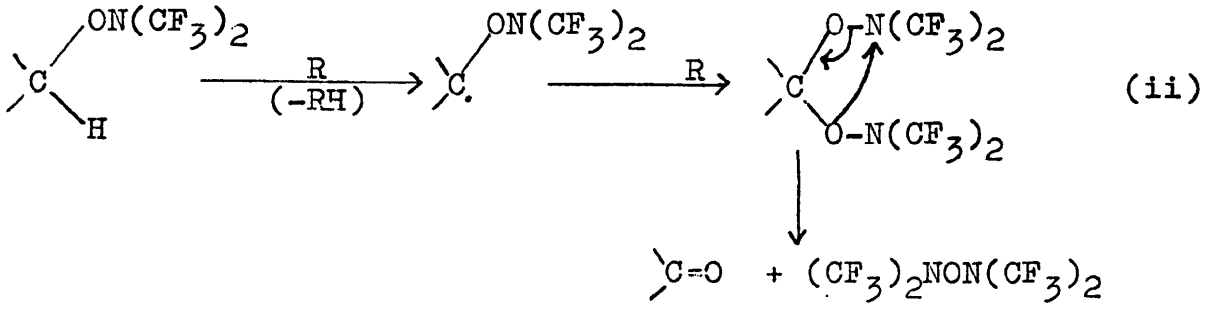
It was also found that further reaction of the oxyl with the monosubstitution products gave ester-type products, e.g.

$$CH_3CH_2ON(CF_3)_2 + 3(CF_3)_2NO\cdot \longrightarrow (CF_3)_2NOCOCH_3 + 2(CF_3)_2NOH + (CF_3)_2N\cdot$$

The reaction is considered to involve a radical mechanism via one or both of the steps outlined below, i.e. [where R= $(CF_3)_2NO$]



(i)



(ii)

Where an allylic hydrogen is available for abstraction, the allylic substitution product may be formed rather than the 2:1 adduct,[82,84] e.g.

$$Me_2CHCH{:}CH_2 + (6) \longrightarrow Me_2\overset{ON(CF_3)_2}{\overset{|}{C}}CH{:}CH_2 + Me_2C{:}CHCH_2ON(CF_3)_2$$

$$CH_2{:}CHSiMe_2H + (6) \longrightarrow CH_2{:}CHSiMe_2ON(CF_3)_2$$

In the reaction of the oxyl with isobutane in carbon tetrachloride solution the yield of allylic substitution product increased as the concentration of reactants decreased.[83] It was considered that this was because addition of the oxyl to the alkene intermediate $Me_2C{:}CH_2$ was reversible, whereas hydrogen abstraction was not, and consequently the yield of allylic substitution product increased as the concentration of reactants decreased, i.e. [where R= $(CF_3)_2NO$]

$$Me_2C{:}CH_2 \underset{}{\overset{R\cdot}{\rightleftharpoons}} Me_2\dot{C}CH_2ON(CF_3)_2$$

$$Me_2C{:}CH_2 \xrightarrow{R(-RH)} \overset{\cdot}{C}H_2\text{-}\overset{Me}{\overset{|}{C}}\text{-}CH_2 \xrightarrow{R\cdot} (CF_3)_2NOCH_2CMe{:}CH_2$$

The reactions of the oxyl with perfluoroalkynes and acetylene have been investigated and found to give α,β-dicarbonyl compounds[85], e.g.

$$4(CF_3)_2NO\cdot + CF_3C{:}{:}CCF_3 \longrightarrow CF_3COCOCF_3 + 2(CF_3)_2NON(CF_3)_2$$

Reaction of the oxyl with the elements mercury,[86] lead,[80] tin,[87] selenium, and bismuth[88] yield crystalline salts of formula $(CF_3)_2NOMON(CF_3)_2$. The salts of sodium, arsenic, and bismuth are also formed by the radical displacement reaction of the oxyl with the appropriate metal halide.[88]

The mercury and sodium salts are useful in the synthesis of amino-oxy substituted organic compounds,[86,89] e.g.

$$Me_3SiCl + [(CF_3)_2NO]_2Hg \longrightarrow (CF_3)_2NOSiMe_3$$

$$NaON(CF_3)_2 + CH_3I \longrightarrow (CF_3)_2NOCH_3$$

Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)

Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (7) was first prepared by Haszeldine and Tipping[90] by irradiation of gaseous tris(trifluoromethyl)hydroxylamine. The proposed mechanism involved N-O fission and subsequent attack of $(CF_3)_2N\cdot$ radicals on the hydroxylamine at oxygen with displacement of a $CF_3\cdot$ radical, i.e.

$$(CF_3)_2NOCF_3 \xrightarrow{u.v.} (CF_3)_2N\cdot + CF_3O\cdot$$

$$(CF_3)_2N\cdot + (CF_3)_2NOCF_3 \longrightarrow (CF_3)_2NON(CF_3)_2 + CF_3\cdot$$

(7)

It has since been reported[81] that reaction of the oxyl (6) with trifluoronitrosomethane gives the oxadiazapentane (7) in high yield (ca. 99%). The suggested mechanism involved radical attack on the nitroso compound at nitrogen, i.e.

$$(CF_3)_2NO\cdot + CF_3NO \longrightarrow CF_3\overset{O\cdot}{N}ON(CF_3)_2 \longrightarrow (CF_3)_2N\cdot + CF_3NO_2$$

$$(CF_3)_2NO\cdot + (CF_3)_2N\cdot \longrightarrow (CF_3)_2NON(CF_3)_2$$

The oxadiazapentane (7) is a colourless liquid (b.p. 48-49 °C) which slowly decomposes at room temperature to give the oxyl (6) and the corresponding hydrazine, i.e.

$$(CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2NO\cdot + (CF_3)_2N\cdot$$

$$2(CF_3)_2N\cdot \longrightarrow (CF_3)_2NN(CF_3)_2$$

The oxadiazapentane (7) reacts with olefins to form 1:1 adducts,[90-92]

$$CF_2{:}CHF + (CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2NCHFCF_2ON(CF_3)_2 \quad (80\%)$$

$$+ (CF_3)_2NCF_2CHFON(CF_3)_2 \quad (20\%)$$

although with an excess of olefin, polymers may be formed.[93] With unsymmetrical olefins the $(CF_3)_2N$ group becomes preferentially attached to that carbon atom of the olefin known to be more susceptible towards free-radical attack. The reaction with olefins is believed to involve a radical chain mechanism, i.e.

$$(CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2N\cdot + (CF_3)_2NO\cdot$$

$$(CF_3)_2N\cdot + \rangle C{:}C\langle \longrightarrow (CF_3)_2N\overset{|}{C}\text{-}\dot{C}\text{-}$$

$$\downarrow (7)$$

$$(CF_3)_2N\overset{|}{C}\text{-}\overset{|}{C}ON(CF_3)_2$$

$$+ (CF_3)_2N\cdot \longrightarrow \underline{\text{etc}}.$$

The remarkable aspect of such additions is the apparent exclusive attack of the intermediate radicals $(CF_3)_2N\overset{|}{C}\text{-}\dot{C}\text{-}$ at the oxygen atom of (7) in the chain-transfer step.

With suitable olefins, e.g. CHR:CHR', a mixture of the erythro- and threo-adducts is formed, thus indicating that addition does not involve a four-centre transition state.

Where an allylic hydrogen atom is available for abstraction the allylic substitution product may be formed, together with the 1:1 adduct[84], e.g.

$$MeCH{:}CHSiCl_3 + (CF_3)_2N\cdot \longrightarrow \dot{C}H_2CH{:}CHSiCl_3 + (CF_3)_2NH$$

$$\dot{C}H_2CH{:}CHSiCl_3 + (7) \longrightarrow (CF_3)_2NOCH_2CH{:}CHSiCl_3 + (CF_3)_2N\cdot$$

The $(CF_3)_2N\cdot$ radical is believed to be highly electrophilic and comparable to the $CF_3\cdot$ radical although being bulkier it is more subject to steric effects.[92]

DISCUSSION

The purpose of this work was to study the reactions of bistrifluoromethylamino-oxyl (6) and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (7) with certain organic compounds with respect to free-radical rearrangements. Although any classification of free-radical rearrangements is rather arbritary as a certain amount of overlap is bound to occur, the discussion has been broadly divided into four main areas;

A. 1,2-Shifts

B. Intramolecular fragmentation

C. Cyclisation

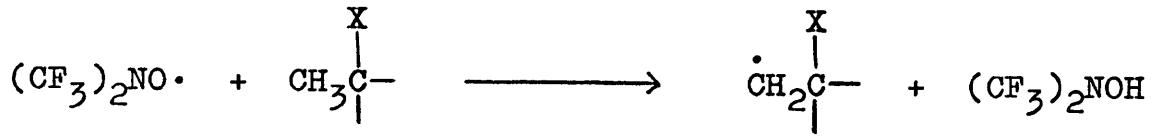
D. Allylic migration

A. 1,2-Shifts

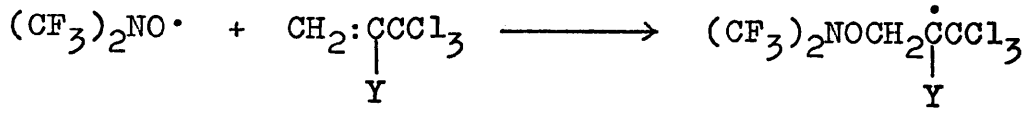
1. Halogen migration

True examples of halogen migrations are mainly limited to 1,2-shifts of chlorine. The transition state involved in the rearrangement step requires an octet expansion to accomodate the extra electron and so precludes the 1,2-shift of fluorine. The rearrangements of bromoalkyl radicals are complicated by their intermolecularity, i.e. they may occur via an elimination/addition process, due to the ease of the β-scission of bromine, and as a result there are relatively few authentic examples of the intramolecular rearrangement of bromine.

The radical intermediates in this study were generated by the reaction of the oxyl (6) with (a) halogenoalkanes, where hydrogen abstraction by the oxyl on compounds of type $CH_3CX<$ gave a primary radical, i.e. (where X= Br or Cl)



and (b) chloroalkenes, where the addition of the oxyl (6) generated a secondary or tertiary radical depending on the nature of the group Y, i.e. (where Y= H or Me)



The reactions were carried out in the dark using neat mixtures of the oxyl and the halide, and in certain cases, the experiments were repeated in the gas phase.

As a comparison several reactions were carried out with the oxadiazapentane (7), again using neat mixtures of reactants.

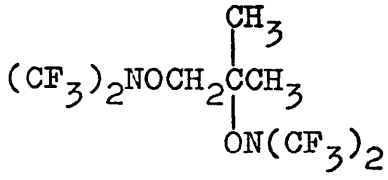
The ^{19}F n.m.r. spectra are recorded in p.p.m. relative to $CF_3SCH_2CHBrCH_2Br$ reference, and are followed by the approximate shifts relative to T.F.A. reference at 0.0 p.p.m., except where stated.

(a) The reactions of the oxyl (6) with halogenoalkanes

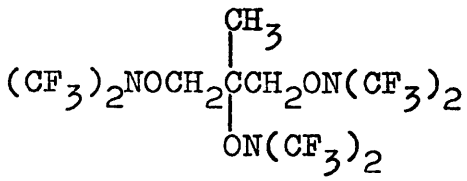
(i) With t-butyl bromide

A 2:1 molar mixture of the oxyl and t-butyl bromide on reaction at room temperature (30h) gave NN-bistrifluoromethylhydroxylamine (41% based on oxyl), unchanged t-butyl bromide (25% recovered), several minor unidentified products, 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methylpropane (8) (10% based on consumed alkane), 1,2,3-tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane (9) (10% based on consumed alkane), 1-(NN-bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane (10) (33.5% based on consumed alkane),

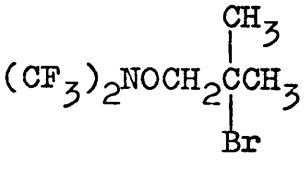
1,2-bis(NN-bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane (11) (15.5% based on alkane) and 1,2-dibromo-2-methylpropane (12) (26.5% based on alkane).



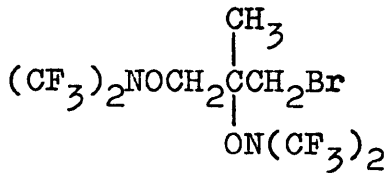
(8)



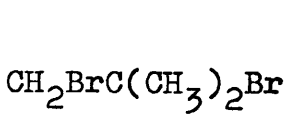
(9)



(10)



(11)



(12)

The three amino-oxy derivatives (9-11) were identified by elemental analysis and the spectroscopic data outlined below. The other compounds are known compounds [compound (8) having been made previously by the reaction of the oxyl (6) with isobutene [82]], and were identified by a comparison of their i.r., n.m.r., and mass spectra with those of authentic samples.

1,2,3-Tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane (9)

The i.r. spectrum of the compound showed absorptions typical of an amino-oxy substituted alkane at 3.31-3.45 (C-H str.), 7.69-8.30 (C-F str.), 9.41 (C-O-N str.), 10.35 (C-N str.), and 14.08 (CF_3 def.) μm.

The ^{1}H n.m.r. spectrum showed absorptions at δ-6.0 (3H, s), -3.25 (2H, AB, J=11Hz), and -3.15 (2H, AB) p.p.m. (relative to p-$Cl_2C_6H_4$), assigned to the methyl protons and to the methylene protons in the

two $-CH_2ON(CF_3)_2$ groups, respectively. The non-equivalence of the methylene protons in each group is probably due to hindered rotation of the bulky amino-oxy groups.

The ^{19}F n.m.r. spectrum showed two singlet absorptions at δ -7.5 and -9.5 p.p.m. (relative to T.F.A.), integrated intensities 2:1, assigned to the fluorines in the two $-CH_2ON(CF_3)_2$ groups and in the $\geq CON(CF_3)_2$ group, respectively.

The mass spectrum showed peaks at m/e 391 {1.5%, $[M-(CF_3)_2NO]^+$}, 377 {5%, $[M-CH_2ON(CF_3)_2]^+$}, 223 (1%, $C_6H_7F_6NO^+$), 182 [12%, $-CH_2ON(CF_3)_2^+$], and 69 (33%, CF_3^+).

1-(NN-bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane (10)

The i.r. spectrum of the compound showed only that it was an amino-oxy-substituted alkane.

The ^1H n.m.r. spectrum showed singlet absorptions at δ -5.7 and -3.8 p.p.m. (relative to p-$Cl_2C_6H_4$), integrated intensities 3:1, assigned to six methyl protons and the protons in a $-CH_2ON(CF_3)_2$ group, respectively, while the ^{19}F n.m.r. spectrum showed a singlet absorption at δ -11.3 p.p.m. (relative to T.F.A.), assigned to the fluorines in an amino-oxy group.

Confirmation of the non-rearranged structure was obtained from the mass spectrum which showed peaks at m/e 303 (34%, M^+), 288 [5%, $(M-CH_3)^+$], 222 [3.5%, $(M-Br)^+$], 182 {4%, $[CH_2ON(CF_3)_2]^+$}, 135 (2%, $C_4H_8Br^+$), and 121 (7%, $C_3H_6Br^+$).

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane (11)

The i.r. spectrum of the compound showed only that it was an amino-oxy-substituted alkane.

The ^1H n.m.r. spectrum showed absorptions at δ 1.35 (3H, s), 3.27 (1H, AB, J= 11Hz), 3.43 (1H, AB), and 4.14 (2H, s) p.p.m., assigned to a $-CH_3$ group, the two non-equivalent protons in a $-CH_2Br$ group, and a $-CH_2ON(CF_3)_2$ group, respectively.

The ^{19}F n.m.r. spectrum showed a singlet at δ 42.37 (6F) and a broad singlet at 40.56 (6F) p.p.m. (relative to p-$CF_2ClSC_6H_4Cl$), assigned to the fluorines in the $-CH_2ON(CF_3)_2$ and $>CON(CF_3)_2$ groups, respectively.

The mass spectrum showed peaks at m/e 377 [4%, $(\underline{M}-CH_2Br)^+$] 302 {3%, $[\underline{M}-ON(CF_3)_2]^+$}, 288 {10%, $[\underline{M}-CH_2ON(CF_3)_2]^+$}, 182 [3%, $CH_2ON(CF_3)_2^+$], 93 (4%, CH_2Br^+), and was identical to that previously reported.[95]

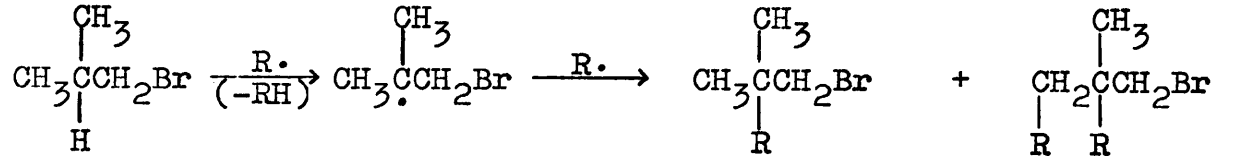
The formation of the products may be explained by the mechanism outlined in Scheme 1. Initial hydrogen abstraction by the oxyl gives intermediate (13) which may be scavenged by the oxyl to give the non-rearranged product (10).

Alternatively, an intramolecular 1,2-shift of bromine may occur to give the relatively more stable intermediate (14)(route 1). The isolation of the 1,2-dibromo-(12)- and 1,2-bis(amino-oxy)-(8)-adducts, however, suggests that an intermolecular mechanism, involving the elimination and addition of bromine (route 2) occurs to a considerable extent.

None of the monosubstituted rearranged isomer (15) was detected in the reaction products, indicating that rather than couple with the oxyl, the rearranged intermediate (14) preferentially undergoes further hydrogen abstraction by

the oxyl to give the bromo-olefin which is then scavenged by the oxyl to give the disubstituted product (11).

However, a previous investigation of the reaction of the oxyl with isobutylbromide, which presumably involves the intermediate (14), has been reported[95] to give the mono- (15) and bis(amino-oxy)- (11) adducts in the ratio ca. 8:1, i.e. [where R = $(CF_3)_2NO$]



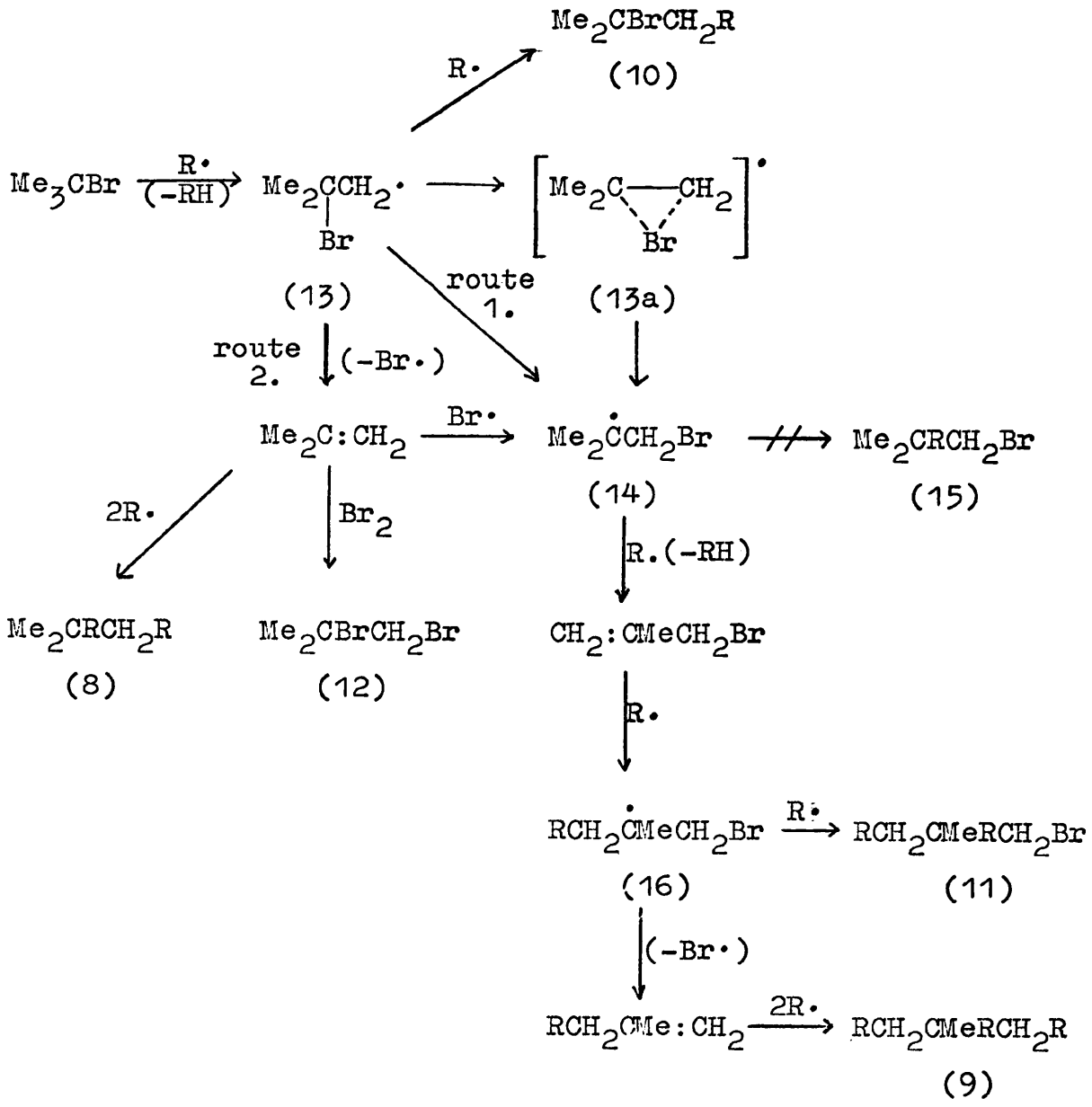
(14) (15) (78%) (11) (10%)

As no products arising from loss of bromine were reported, the assumption that intermediate (14) is common to both reactions may not be valid.

A more accurate description for the intermediate involved may be the bridged structure (13a), the rate of formation of which would be expected to be slower from the tertiary radical (14) than from the relatively less stable primary radical (13).

The tri(amino-oxy)-substituted product (9) is probably formed via β-scission of bromine from the intermediate (16), giving the monosubstituted olefin which is then further scavenged by the oxyl. An alternative mechanism involving allylic hydrogen abstraction by the oxyl on the isobutene formed in situ is less probable, as the concentration of olefin is unlikely to be very high, and therefore abstraction is unfavoured.

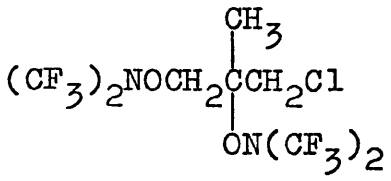
Reaction of the oxyl with t-butyl bromide



Scheme 1. [where R = $(CF_2)_2NO$]

(ii) With t-butyl chloride

The reaction of a 2:1 molar mixture of the oxyl and t-butyl chloride at room temperature (13d) gave hydrogen chloride (ca. 61% based on consumed alkane), NN-bistrifluoromethylhydroxylamine (ca. 13% based on oxyl), unchanged t-butyl chloride (30% recovered), several unidentified products, 1,2-(NN-bistrifluoromethylamino-oxy)-2-methylpropane (8) (37% based on consumed alkane), 1,2,3-tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane (9) (8% based on consumed alkane), and 1,2-bis(NN-bistrifluoromethylamino-oxy)-3-chloro-2-methylpropane (17) (3.5% based on alkane).



(17)

The disubstituted chloroalkane (17) was identified by the spectroscopic data outlined below. The bis- and tri-(amino-oxy) products (8) and (9) were identified by comparing their i.r., n.m.r., and mass spectra with those previously obtained (see p. 36).

1,2-bis(NN-bistrifluoromethylamino-oxy)-3-chloro-2-methylpropane (17)

The i.r. spectrum showed only that the compound was an amino-oxy-substituted alkane with absorptions at 3.33-3.42 (C-H str.), 7.66-8.26 (C-F str.), 9.38 or 9.49 (C-O-N str.), 10.31 (C-N str.), and 13.97 (CF_3 def.) μm.

The ^1H n.m.r. spectrum showed absorptions at δ 1.22

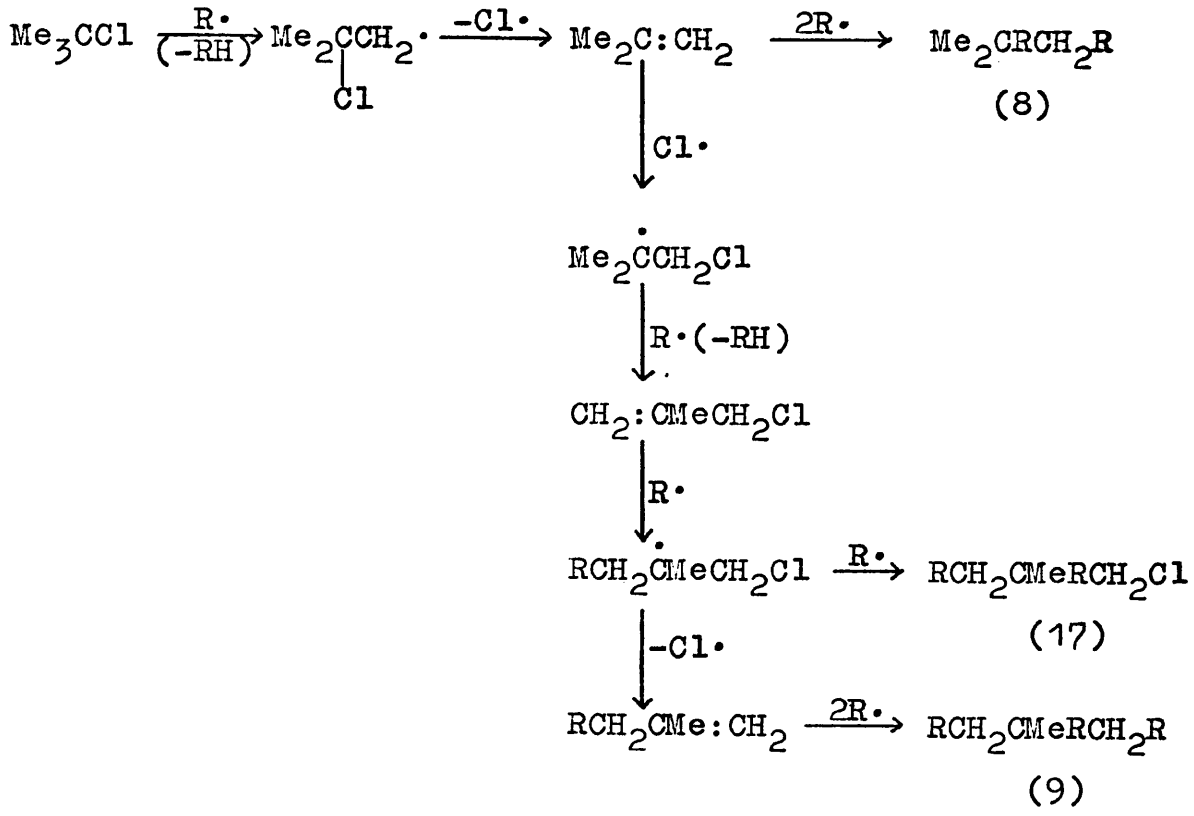
(3H, s), 3.32 (1H, AB, J= 12Hz), 3.44 (1H, AB), and 4.03 (2H, s) p.p.m., assigned to a $-CH_3$ group, the two non-equivalent protons in a $-CH_2Cl$ group (adjacent to an asymmetric centre), and the $-CH_2ON(CF_3)_2$ group, respectively.

The ^{19}F n.m.r. spectrum showed a singlet at δ 42.65 and a broad singlet at 40.82 p.p.m. (relative to p-$CF_2ClSC_6H_4Cl$), integrated intensities 1:1, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ group, and the relatively more hindered $\rightarrow CON(CF_3)_2$ group, respectively.

The mass spectrum was virtually identical to that reported by O'Connor[95] and showed peaks at m/e 411 [1%, $(M-CH_3)^+$], 377 [9%, $(M-CH_2Cl)^+$], 258 {12%, $[M-(CF_3)_2NO]^+$}, 244 {16%, $[M-(CF_3)_2NOCH_2]^+$}, 182 [16%, $(CF_3)_2NOCH_2^+$], and 49 (14%, CH_2Cl^+).

The product mixture was rather more complex than that obtained from the bromide, but the isolation of the 1,2-bis(amino-oxy) adduct (8) indicates that a similar mechanism occurs, involving an elimination/addition pathway, with the free chlorine competing with the oxyl as a chain carrier in the hydrogen-abstraction step. Although the elimination of chlorine from an alkyl radical is generally less favourable than for bromine, particularly at room temperature, it appears that this behaviour is common in the reactions of the oxyl with chloroalkanes (e.g. 2,2-dichloropropane and 2-chloro-2-phenylpropane; see later p. 44 and p. 47)

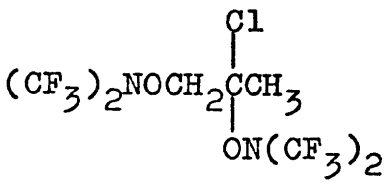
The products (9) and (17) are postulated to arise via a mechanism similar to that suggested for the bromide, i.e. [Scheme 2; where R = $(CF_3)_2NO$]



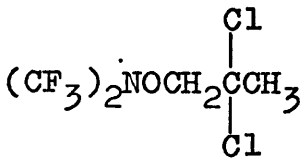
Scheme 2

(iii) With 2,2-dichloropropane

A 2:1 molar mixture of the oxyl and 2,2-dichloropropane on reaction at 70-80 °C (78d) gave a lower-boiling fraction which contained hydrogen chloride, NN-bistrifluoromethylamine, and carbon dioxide, and a higher-boiling mixture which contained NN-bistrifluoromethylhydroxylamine (ca. 32% based on oxyl), unchanged chloride (ca. 50% recovered), five unidentified products, 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-chloropropane (18) (ca. 24% based on consumed alkane), and a compound tentatively identified as 1-(NN-bistrifluoromethylamino-oxy)-2,2-dichloropropane (19) (ca. 42%). The i.r. spectrum of the higher-boiling mixture showed absorptions in the region 5.45-5.85 (C:O str.) μm.



(18)



(19)

The reaction was repeated at room temperature (440d), again using a 2:1 molar mixture of the oxyl and the chloride and gave hydrogen chloride, NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, unchanged chloride, two unidentified products, 1-(NN-bistrifluoromethylamino-oxy)-2,2-dichloropropane (19) (ca. 38%) and 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-chloropropane (18) (ca. 40%). Once again the i.r. spectrum of the higher-boiling mixture showed a strong absorption in the region 5.45-5.85 (C:O str.) μm.

The bis(amino-oxy)-adduct (18) was identified by elemental analysis and the spectroscopic data outlined below. The monosubstituted product (19) was isolated contaminated with unchanged dichloropropane, and was identified from spectral data obtained on the two-component mixture.

1,2-bis(NN-bistrifluoromethylamino-oxy)-2-chloropropane (18)

The i.r. spectrum showed absorptions at 3.33-3.46 (C-H str.), 7.63-8.24 (C-F str.), 9.36 or 9.54 (C-O-N str.), 10.29 (C-N str.), and 14.03 (CF_3 def.) μm.

The ^{1}H n.m.r. spectrum showed absorptions at δ 1.68 (3H, s), 3.96 (1H, AB, J= 10Hz), and 4.14 (1H, AB) p.p.m., assigned to the $-CH_3$ and the non-equivalent protons in the $-CH_2ON(CF_3)_2$ group, respectively. The ^{19}F n.m.r. spectrum showed (i) a singlet absorption at δ 30.09 (-7.2) p.p.m., and

(ii) two quartets at δ 27.6 (-9.7) and 26.9 (-10.4) p.p.m. (J= 11Hz), integrated intensities 1:1, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ group and the non equivalent CF_3 groups in the $(CF_3)_2NOC<$ group, respectively.

The mass spectrum showed peaks at m/e 377 [1%, $(\underline{M}-Cl)^+$], 244 {20%, $[\underline{M}-(CF_3)_2NO]^+$}, 230 {6%, $[\underline{M}-(CF_3)_2NOCH_2]^+$}, 209 (1%, $C_5H_5F_6NO^+$), 182 [1%, $(CF_3)_2NOCH_2^+$], and 76 (7%, $C_3H_5Cl^+$).

1-(NN-bistrifluoromethylamino-oxy)-2,2-dichloropropane (19)

The i.r. spectrum of the compound was not recorded, since it could not be obtained pure.

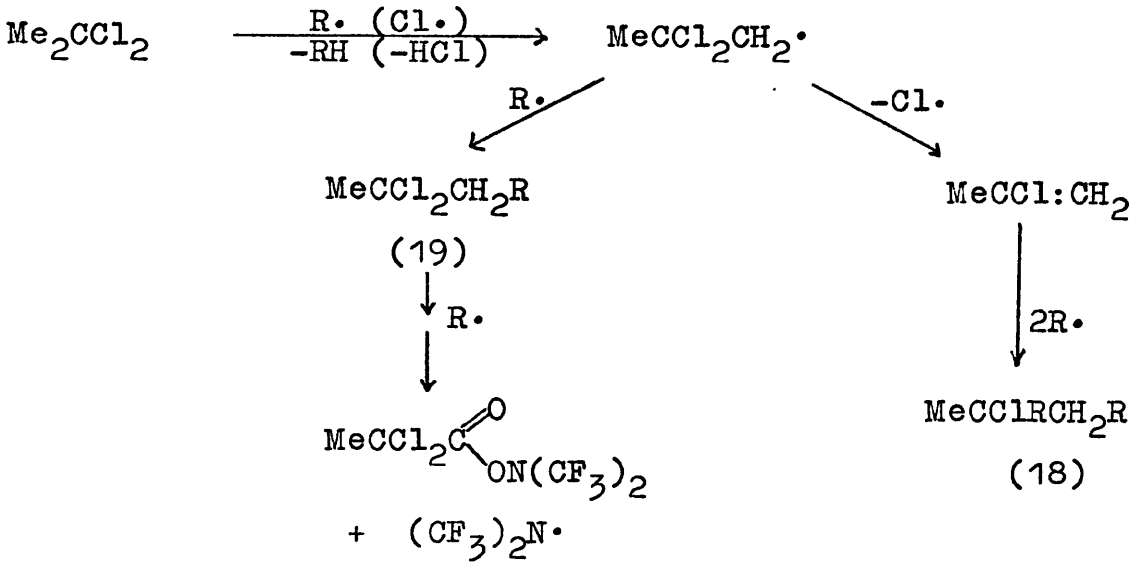
The ^1H n.m.r. spectrum showed absorptions at δ 1.91 (3H, s) and 4.12 (2H, s) p.p.m., assigned to the $-CH_3$ and $-CH_2ON(CF_3)_2$ group, respectively. A singlet absorption was observed in the ^{19}F n.m.r. spectrum at δ 29.1 (-8.2) p.p.m., typical of the fluorines in an amino-oxy group.

The mass spectrum showed peaks at m/e 263 (1%, $C_4HCl_2F_6NO^+$), 243 [7%, $(\underline{M}-HCl)^+$], 182 [1%, $(CF_3)_2NOCH_2^+$], 111 (77%, $C_3H_5Cl_2^+$), 97 (100%, $C_2H_3Cl_2^+$), 75 (71%, $C_3H_4Cl^+$), and 69 (91%, CF_3^+).

Although the yields of hydrogen chloride were not determined, the formation of the dehydrochlorinated adduct (18) indicates that loss of chlorine occurs to a considerable extent both at 70-80 °C and at room temperature.

The presence of NN-bistrifluoromethylamine and a carbonyl absorption in the i.r. spectra of the higher-boiling mixtures indicate that further attack of the oxyl at C_1 probably occurs; such further attack of the oxyl to form carbonyl products is common in the reactions of the oxyl with

relatively unreactive alkanes, i.e. [where R = $(CF_3)_2NO$]

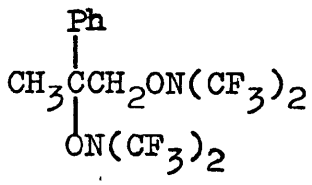


(iv) With 1,1,1-trichloroethane

The reaction of a 2:1 molar mixture of the oxyl and 1,1,1-trichloroethane gave ca. 95% recovered trichloroethane after storage at room temperature (260d) and at 70-80 °C (240d), probably due to the low reactivity of the primary hydrogens towards the electrophilic oxyl.

(v) With 2-chloro-2-phenylpropane

A 2:1 molar mixture of the oxyl and the chloride on reaction at room temperature (35min) gave hydrogen chloride (97.5% based on consumed chloride), NN-bistrifluoromethylhydroxylamine (12.5% based on oxyl), NN-bistrifluoromethylamine (trace), unchanged 2-chloro-2-phenylpropane (32.5% recovered), several minor unidentified products, and 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-phenylpropane (20) (78% based on consumed chloride), which was identified by elemental analysis and the spectroscopic data outlined below.



(20)

The i.r. spectrum of the major product (20) showed absorptions at 3.22-3.47 (C-H str.), 6.24-6.92 (C:C str.), 7.72-8.30 (C-F str.). 9.46 (C-O-N str.), 10.37 (C-N str.), 13.04 (C-H def.), and 14.39 and 14.12 (CF_3 def. and/or C-H def.) μm.

The ^1H n.m.r. spectrum showed absorptions at δ 1.47 (3H, s), 3.75 (1H, AB, J= 10Hz), 4.01 (1H, AB), and ca. 6.94 (5H, c) p.p.m., assigned to the $-CH_3$ group, the two non-equivalent protons in the $-CH_2ON(CF_3)_2$ group, and the Ph group, respectively.

The ^{19}F n.m.r. spectrum showed a singlet at δ 29.7 (-7.6) p.p.m., and a broad complex absorption at δ ca. 27.4 (-9.9) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ group, and the $PhC(ON(CF_3)_2)$ group, respectively.

The mass spectrum showed peaks at m/e 286 {43%, $[M-(CF_3)_2NO]^+$}, 272 {10%, $[M-(CF_3)_2NOCH_2]^+$}, 182 [1%, $(CF_3)_2NOCH_2^+$], 134 (74%, $C_9H_{10}O^+$), 118 (100%, $C_9H_{10}^+$), and 77 (22%, $C_6H_5^+$).

The formation of the dehydrochlorinated compound (20) indicates that β-scission of chlorine from intermediate (21) to give the conjugated olefin, $MeCPh:CH_2$, precludes the rearrangement of phenyl or chlorine, despite the fact that

a 1,2-shift of chlorine would generate a benzylic radical, i.e. [where R = $(CF_3)_2NO$]

$$Me_2CPhCl \xrightarrow[(-RH \text{ or } HCl)]{R\cdot \text{ or } Cl\cdot} MeCPhClCH_2\cdot \quad (21)$$

$$(21) \xrightarrow{-Cl\cdot} MeCPh{:}CH_2 \xrightarrow{2R\cdot} MeCPhRCH_2R \quad (20)$$

The olefin is then quickly scavenged by the oxyl to form the disubstituted adduct (20). The liberated chlorine competes with the oxyl in the initial hydrogen abstraction step to give hydrogen chloride.

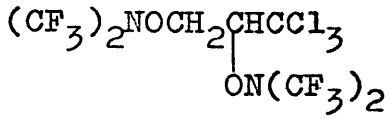
The rate of reaction was faster than one would expect for abstraction of a primary hydrogen with electron-withdrawing β-substituents and this is discussed later (p. 62).

(b) The reactions of the oxyl (6) with chloroalkenes

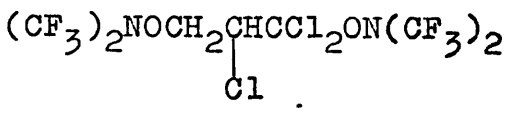
(i) With 3,3,3-trichloropropene at room temperature

A 2:1 molar mixture of the oxyl and 3,3,3-trichloropropene on reaction at room temperature (6d) gave 1,2-bis(NN-bistrifluoromethylamino-oxy)-3,3,3-trichloropropane (22) (97% based on alkene), which was identified by elemental analysis and spectroscopic data, 1,3-bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane (23) (2.5% based on alkene), which was identified by g.l.c. analysis (see p. 50), and minor quantities of recovered olefin, NN-bistrifluoromethylamine, and NN-bistrifluoromethyl-

hydroxylamine.



(22)



(23)

The i.r. spectrum of the major product (22) showed absorptions at 7.69-8.29 (C-F str.), 9.42 and 9.55 (C-O-N str.), 10.35 (C-N str.), and 14.08 (CF_3 def.)μm, typical of an amino-oxy group, and bands at 3.33-3.44 (C-H str.), and 11.89-12.66 (C-Cl str.)μm.

The ^1H n.m.r. spectrum showed a complex absorption at δ ca. 4.7 p.p.m, assigned to both the methylene and methine protons. The ^{19}F n.m.r. spectrum showed a singlet at δ 28.16 (-9.8) p.p.m. and a broad singlet at δ 26.7 (-11.3) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ group and in the sterically hindered $>CHON(CF_3)_2$ group, respectively.

The mass spectrum showed peaks at m/e 363 [7%, $(M-CCl_3)^+$], 312 {<1%, $[M-(CF_3)_2NO]^+$}, 182 (100%, $CH_2ON(CF_3)_2^+$), 144 (13%, $C_3H_3Cl_3^+$), and 117 (8%, CCl_3^+).

(ii) With 3,3,3-trichloropropene at 70-80 °C

A 2:1 molar mixture of the oxyl and the chloride on reaction in the gas phase at 70-80 °C (6d) gave 1,3-bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane (23) (77% based on alkene), which was identified by elemental analysis and spectroscopic data, and 1,2-bis(NN-bistrifluoromethylamino-oxy)-3,3,3-trichloropropane (22) (15% based on alkene), which was identified by g.l.c. analysis. Minor amounts of recovered oxyl and NN-bistrifluoromethylhydroxylamine were

also detected in the products.

The i.r. spectrum of the rearranged adduct (23) showed the characteristic absorptions of the amino-oxy group at 7.66-8.29 (C-F str.), 9.35 and 9.52 (C-O-N str.), 10.31 (C-N str.), and 13.99 (CF_3 def.)μm, together with bands at 3.34-3.44 (C-H str.), and 11.36-12.24 (C-Cl str.)μm.

The ^{1}H n.m.r. spectrum showed absorptions at δ ca. 4.32 (2H, c) and 4.68 (1H, dd, J= 9Hz,2Hz) p.p.m., assigned to the $-CH_2ON(CF_3)_2$ group and the >CHCl group, respectively.

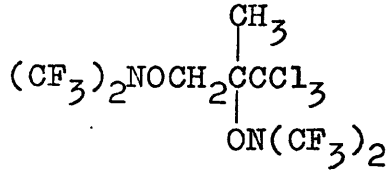
The ^{19}F n.m.r. spectrum showed two singlets at δ 29.5 (-7.8) and 25.4 (-11.9) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ group and $(CF_3)_2NOCCl_2$ group, respectively.

Confirmation of the structure was obtained from the mass spectrum which showed peaks at m/e 445 [1%, $(M-Cl)^+$], 312 {39%, $[M-(CF_3)_2NO]^+$}, 250 [19%, $(CF_3)_2NOCCl_2^+$], 230 {4%, $[M-(CF_3)_2NOCCl_2]^+$}, 182 [58%, $(CF_3)_2NOCH_2^+$], and 144 (20%, $C_3H_3Cl_3^+$).

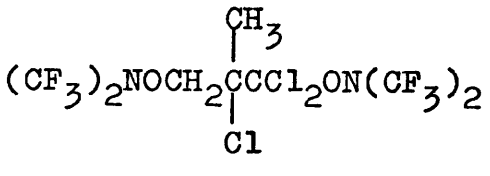
(iii) With 3,3,3-trichloro-2-methylpropene

A 2:1 molar mixture of the oxyl and 3,3,3-trichloro-2-methylpropene on reaction at room temperature (1h) gave unchanged oxyl (ca. 0.5% recovered), hydrogen chloride (ca. 6% based on alkene), NN-bistrifluoromethylhydroxylamine (ca. 5% based on oxyl), a product (A) identified by elemental analysis and spectroscopic data as a mixture of 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methyl-3,3,3-trichloropropane (24) (ca. 56% based on alkene) and 1,3-bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloro-2-methylpropane (25) (ca.

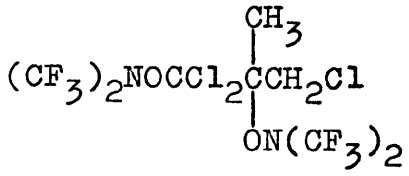
28% based on alkene), a minor product tentatively identified as 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methyl-1,1,3-trichloropropane (26) (9% based on alkene), an unidentified amino-oxy-substituted product (B) (ca. 2% based on alkene), and a minor unidentified product.



(24)



(25)



(26)

The isomers (24) and (25) could not be separated by g.l.c. and their relative yields were estimated from the ^{19}F n.m.r. spectrum of the two-component mixture. The coupled g.l.c./mass spectrum of product (B) showed a base peak at m/e 69 (100%, CF_3^+) indicating that it was probably an amino-oxy derivative.

Product A

The i.r. spectrum showed the characteristic absorptions of an amino-oxy group together with bands at 3.33-3.45 (C-H str.), and 11.95-12.36 (C-Cl str.)μm.

The ^1H n.m.r. spectrum showed (i) two overlapping singlets at δ 1.75 and 1.82 p.p.m., and (ii) two overlapping AB systems centred on δ 4.40 and 4.58 p.p.m., integrated intensities 3:2, assigned to the CH_3 group and $-CH_2ON(CF_3)_2$

group, respectively, in both isomers.

The ^{19}F n.m.r. spectrum showed two singlets at δ 29.4 (-7.9) and 24.9 (-12.4) p.p.m., and a complex absorption at δ ca. 26.6 (-10.6) p.p.m., integrated intensities 3:1:2, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ groups of both isomers, the $-CCl_2ON(CF_3)_2$ group of the rearranged isomer (25), and the $>CON(CF_3)_2$ group (adjacent to an asymmetric centre) of the non-rearranged isomer (24), respectively.

The mass spectrum showed peaks at (i) m/e 459 [9%, $(M-Cl)^+$], 326 {26%, $[M-(CF_3)_2NO]^+$}, 312 {10%, $[M-CH_2ON(CF_3)_2]^+$} 182 [85%, $CH_2ON(CF_3)_2^+$], 158 (35%, $C_4H_5Cl_3^+$), and 144 (28%, $C_3H_3Cl_3^+$), which were assigned to both isomers, (ii) 377 [5%, $(M-CCl_3)^+$], 209 (1%, $C_5H_5F_6NO^+$), and 117 (11%, CCl_3^+), which were assigned to the non-rearranged isomer (24), and (iii) 250 [2%, $CCl_2ON(CF_3)_2^+$], and 244 {6%, $[M-CCl_2ON(CF_3)_2]^+$}, which were assigned to the rearranged isomer (25).

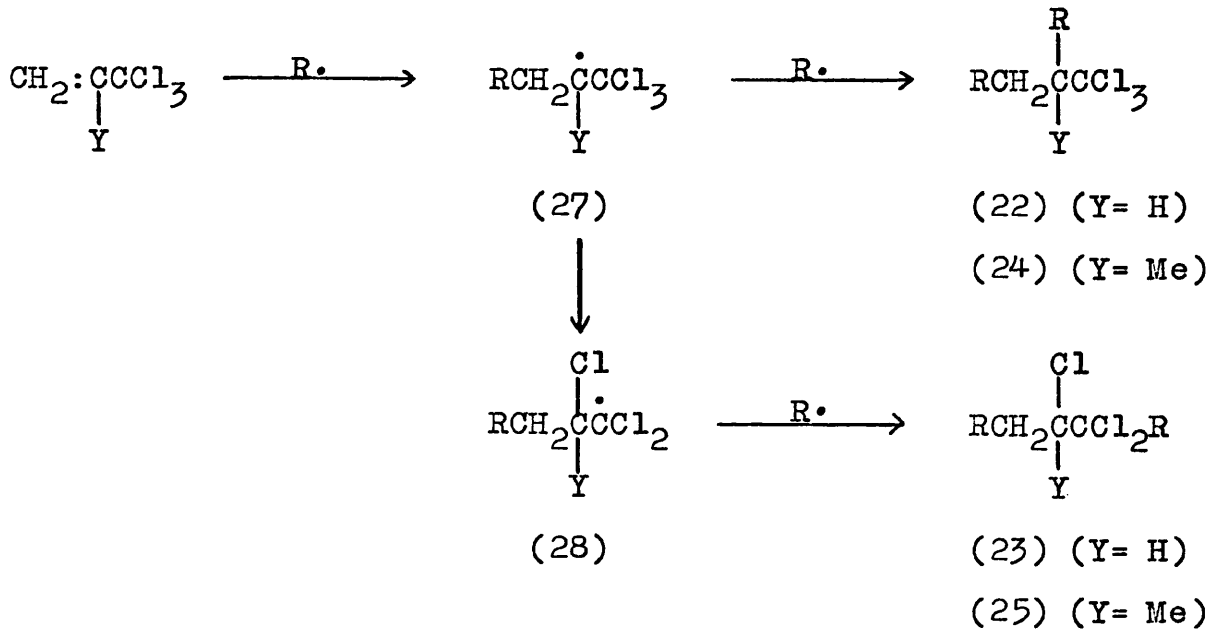
1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methyl-1,1,3-trichloropropane (26)

A pure sample of the compound could not be isolated and it was identified from the n.m.r. spectrum of a mixture of several components.

The ^1H n.m.r. spectrum showed absorptions at δ 1.75 (3H, s) and 3.96 (2H, s) p.p.m., assigned to the CH_3 and $-CH_2Cl$ groups, respectively. The ^{19}F n.m.r. spectrum showed two singlets at δ 26.6 (-10.6) and 24.9 (-12.4) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $>CON(CF_3)_2$ group and the $-CCl_2ON(CF_3)_2$ group, respectively.

Confirmation of the structure was obtained from the g.l.c./mass spectrum which showed peaks at m/e 459 [1%, $(\underline{M}-Cl)^+$], 445 [1%, $(\underline{M}-CH_2Cl)^+$], 326 {30%, $[\underline{M}-(CF_3)_2NO]^+$}, 250 [1.5%, $CCl_2ON(CF_3)_2^+$], 244 {6%, $[\underline{M}-CCl_2ON(CF_3)_2]^+$}, 158 (37%, $C_4H_5Cl_3^+$), and 49 (8.5%, CH_2Cl^+).

The formation of the products in the reaction of the oxyl with trichloropropene can be explained by the mechanism outlined in Scheme 3 [where R = $(CF_3)_2NO$; Y= H]

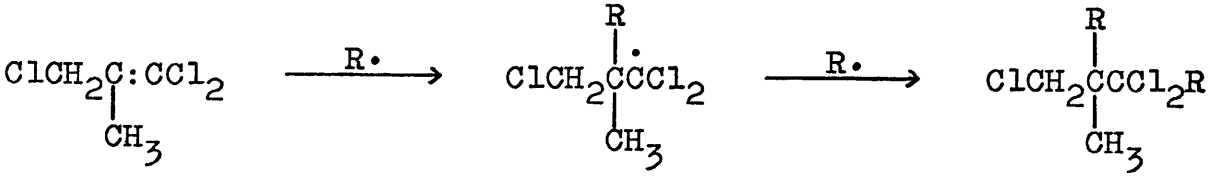


Scheme 3

The intermediate radical (27) may be directly scavenged by the oxyl to give the non-rearranged product (22) or, alternatively, may undergo a 1,2-chlorine shift to give the relatively more stable radical (28), and in the gas-phase reaction, where the relatively lower concentration of reactants and higher temperature favour rearrangement, the rearranged isomer (23) is obtained as the major product.

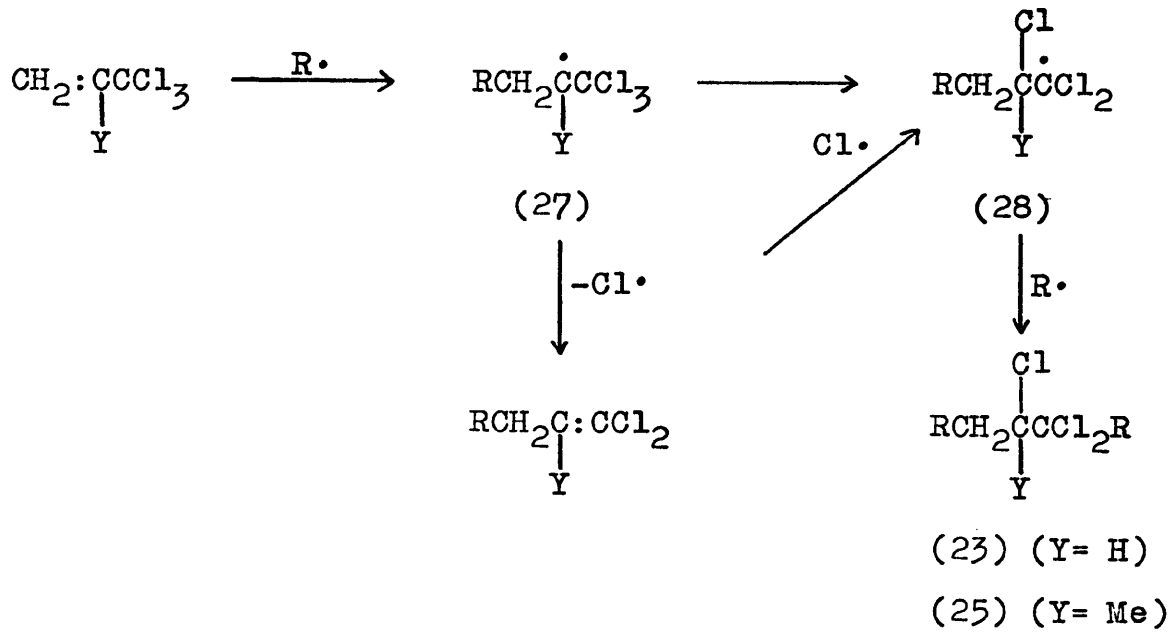
In the reaction of the oxyl with trichloro-2-methylpropene (Scheme 3; Y= CH_3) the rearrangement of the intermediate (27) appears to be relatively more favourable. As the rearrangement in this case involves a tertiary radical, the driving force for rearrangement is presumably less, and the effect is probably explained by steric hindrance at the tertiary carbon radical which prevents chain-transfer with the oxyl to some extent and so favours the rearrangement step.

The 3,3,3-trichloro-2-methylpropene used in the reaction was contaminated with ca. 10% 1,1,3-trichloro-2-methylpropene, and this explains the formation of the minor product (26), i.e. [where R = $(CF_3)_2NO$]



(26)

An alternative mechanism, involving the β-scission of chlorine from the intermediate radical (27) followed by combination to give the more stable radical (28), must also be considered to account for the formation of the rearranged products, i.e (where Y= H or Me)



(23) (Y= H)

(25) (Y= Me)

However, the free chlorine atoms formed in such a process would be expected to react with the starting olefin to some extent resulting in the formation of tetrachloro derivatives. Such products were not observed, so the intramolecular mechanism is more likely.

(c) <u>The reactions of the oxadiazapentane (7) with chloro-alkenes</u>

Rearrangement involving a 1,2-chlorine shift should be more favourable in reactions involving the oxadiazapentane (7) than the corresponding reactions with the oxyl (6), since the chain-transfer step in the former reactions involves fission of the N-O-N bond and so increases the lifetime of the intermediate radical. Furthermore, the formation of rearranged products would provide strong evidence for a radical-chain mechanism.

(i) With 3,3,3-trichloropropene

An equimolar mixture of the oxadiazapentane and 3,3,3-trichloropropene on reaction at room temperature (20h) gave unchanged oxadiazapentane (57% recovered), NN-bistrifluoromethylamine (trace), NN-bistrifluoromethylhydroxylamine (trace), unchanged trichloropropene (56% recovered), and 1-NN-bistrifluoromethylamino-3-(NN-bistrifluoromethylaminooxy)-2,3,3-trichloropropane (29) (93% based on consumed alkene), which was identified by elemental analysis and the spectroscopic data outlined below.

$$(CF_3)_2NCH_2\overset{Cl}{\overset{|}{C}}HCCl_2ON(CF_3)_2$$

(29)

The i.r. spectrum of compound (29) showed absorptions at 3.31-3.35 (C-H str.), 7.28-9.27 (C-F str.), 9.57 or 9.71 (C-O-N str.), 10.38 (C-N str.), 11.90-12.63 (C-Cl str.), and 14.04 (CF_3 def.) μm.

The ^1H n.m.r. spectrum showed absorptions at δ ca. 3.6 (1H, AB d, J= 16Hz, 10Hz), ca. 4.05 (1H, distorted AB), and ca. 4.8 (1H, dd, J= 10Hz, 3Hz) p.p.m. The higher-field signals were assigned to the protons in the $-CH_2N(CF_3)_2$ group which, due to the adjacent asymmetric centre, are non-equivalent and couple with the vicinal methine proton to different extents. The assignment of the lower-field signal was more difficult as the expected chemical shifts of the protons in both the $>CHON(CF_3)_2$ and $>CHCl$ groups of the non-rearranged and rearranged compounds, respectively, are in

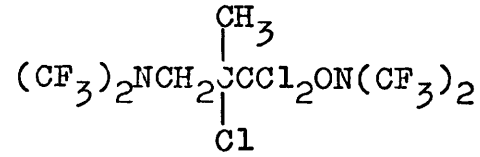
this region and so did not provide conclusive proof for either.

The ^{19}F n.m.r. spectrum showed singlet absorptions at δ 25.4 (-11.9) and 18.6 (-18.6) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $-CCl_2ON(CF_3)_2$ group and $-CH_2N(CF_3)_2$ group, respectively.

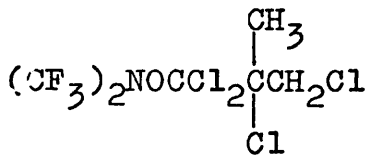
Confirmation of the rearranged structure was obtained from the mass spectrum which showed peaks at m/e 263 (14%, $C_4HCl_2F_6NO^+$), 250 [3.5%, $(CF_3)_2NOCCl_2^+$], 214 {2%, $[M-(CF_3)_2NOCCl_2]^+$}, 166 [100%, $(CF_3)_2NCH_2^+$], and 144 (1%, $C_3H_3Cl_3^+$).

(ii) With 3,3,3-trichloro-2-methylpropene

An equimolar mixture of the oxadiazapentane and 3,3,3-trichloro-2-methylpropene on reaction at room temperature (8d) gave NN-bistrifluoromethylamine, hydrogen chloride, NN-bistrifluoromethylhydroxylamine, ca. nine minor unidentified products, 1-NN-bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2-methyl-2,3,3-trichloropropane (30) (57% based on alkene), and a compound tentatively identified as 1-(NN-bistrifluoromethylamino-oxy)-2-methyl-1,1,2,3-tetrachloropropane (31) (ca. 11.5% based on alkene).



(30)



(31)

The rearranged adduct (30) was identified by elemental analysis and the spectroscopic data outlined below.

The i.r. spectrum showed absorptions at 3.31-3.43 (C-H str.), 7.28-8.59 (C-F str.), 9.72 (C-O-N str.), 10.24 or 10.41 (C-N str.), 11.83-12.38 (C-Cl str.), and 14.04 (CF_3 def.)μm.

The ^1H n.m.r. spectrum showed absorptions at δ 1.81 (3H, s) and 3.93 (2H, bs) p.p.m., assigned to the CH_3 and $-CH_2N(CF_3)_2$ groups, respectively. The ^{19}F n.m.r. spectrum showed singlet absorptions at δ 24.8 (-12.5) and 17.1 (-20.2) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $(CF_3)_2NOCCl_2$ group and the $(CF_3)_2NCH_2$ group, respectively. The chemical shift of the amino-oxy group signal is in the region expected for a $(CF_3)_2NOCCl_2$ group [cf. the rearranged bis(amino-oxy) adduct (25); p. 52] and is slightly downfield of that expected for a $(CF_3)_2NOCMe$ group in the non-rearranged adduct.

Confirmation of the rearranged structure was obtained from the mass spectrum which showed peaks at m/e 277 (14.5%, $C_5H_3Cl_2F_6NO^+$), 275 (1%, $C_6H_5Cl_2F_6N^+$), 228 {6%, $[M-(CF_3)_2NOCCl_2]^+$}, 166 [100%, $(CF_3)_2NCH_2^+$], 158 (5.5%, $C_4H_5Cl_3^+$), and 144 (3%, $C_3H_3Cl_3^+$).

The tetrachloro derivative (31) could not be isolated pure and was identified by the n.m.r. spectrum of a mixture of (31) and an unidentified compound, and by its coupled g.l.c./mass spectrum.

The ^1H n.m.r. spectrum showed absorptions at δ 2.02 (3H, s) and 4.10 (2H, s) p.p.m., assigned to the CH_3 and $-CH_2Cl$ groups, respectively in compound (31), while a singlet absorption was observed in the ^{19}F n.m.r. spectrum at δ 24.1 (-13.2) p.p.m., assigned to the fluorines in a $(CF_3)_2NOCCl_2$

group.

The mass spectrum showed peaks at m/e 326 [100%, $(\underline{M}-Cl)^+$], 312 [2%, $(\underline{M}-CH_2Cl)^+$], 250 [2%, $(CF_3)_2NOCCl_2^+$], 193 (39.5%, $C_4H_5Cl_4^+$), 111 {77%, $[\underline{M}-(CF_3)_2NOCCl_2]^+$}, and 49 (17.5%, CH_2Cl^+).

As expected, the reaction of the oxadiazapentane with trichloropropene resulted in the exclusive formation of rearranged product (29) (Scheme 4; where Y= H), due to the slow rate of chain-transfer of intermediate (32) with the oxadiazapentane, i.e.

$$(CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2N\cdot + (CF_3)_2NO\cdot$$

(7)

$$CH_2{:}C(Y)CCl_3 + (CF_3)_2N\cdot \longrightarrow (CF_3)_2NCH_2\dot{C}(Y)CCl_3$$

(32)

$$(CF_3)_2NCH_2C(Cl)(Y)CCl_2ON(CF_3)_2 \xleftarrow{(7)} (CF_3)_2NCH_2C(Cl)(Y)\dot{C}Cl_2$$

(29) (Y= H)

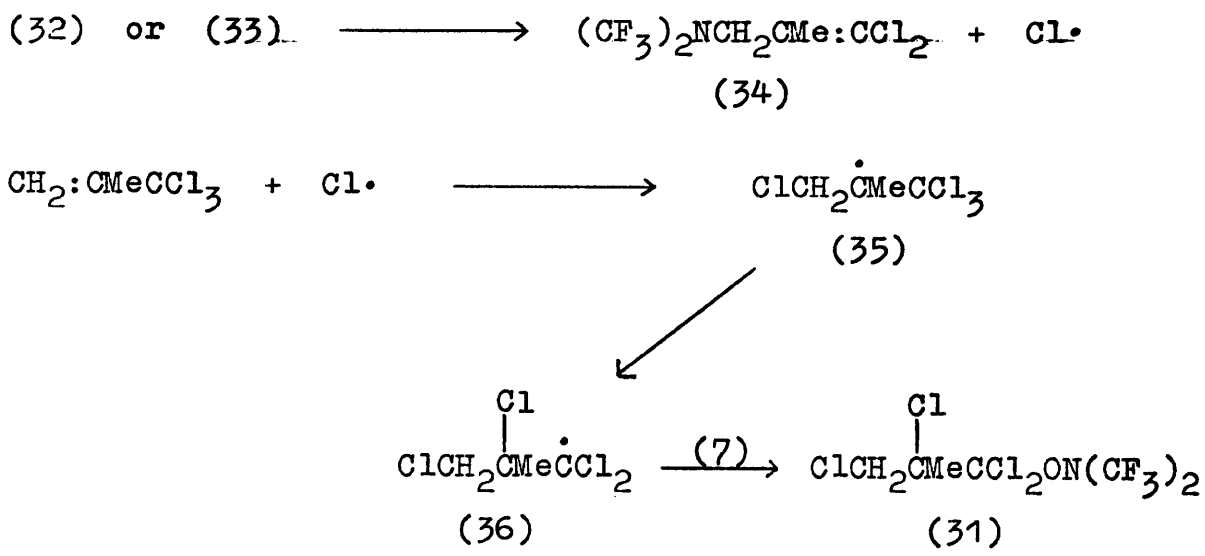
(30) (Y= Me)

(33)

Scheme 4

Similarly, the reaction of the oxadiazapentane with trichloromethylpropene (Scheme 4; where Y= Me) resulted in the formation of the rearranged adduct (30) as the major product. The formation of the other major product, the

tetrachloride (31) can be explained by the mechanism outlined below, i.e.



The fragmentation of allylic chlorine in radical additions to trichloropropene derivatives is favoured as the stability and lifetime of the intermediate radical is increased[29] and is discussed further below. Although the expected olefin intermediate (34) was not isolated, it may have been one of the several minor unidentified products. The chlorine atoms so produced add to the starting olefin to give intermediate (35) which then undergoes rearrangement to give intermediate (36) and chain-transfer to give the tetrachloride (31)

β-Scission of chlorine

1. Chloroalkenes

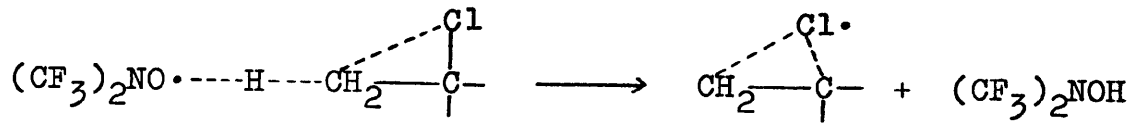
The β-scission of chlorine is less favourable than that of bromine, particularly at room temperature and, as one would expect, products arising from the loss of chlorine were not detected in the reactions of the oxyl with the trichloropropenes. Even at 70-80 °C, where the higher temperature

could favour the fragmentation process, the concentration of oxyl is such that chain-transfer occurs fairly rapidly (as shown by the formation of some non-rearranged adduct) and the loss of chlorine is precluded.

As the stability and lifetime of the intermediate radical is increased, however, fragmentation becomes more favourable, and with the oxadiazapentane, where the chain-transfer step is considerably slower (as shown by the exclusive formation of rearranged products) the β-scission of chlorine from intermediate (32), or the rearranged intermediate (33), competes with chain-transfer to some extent.

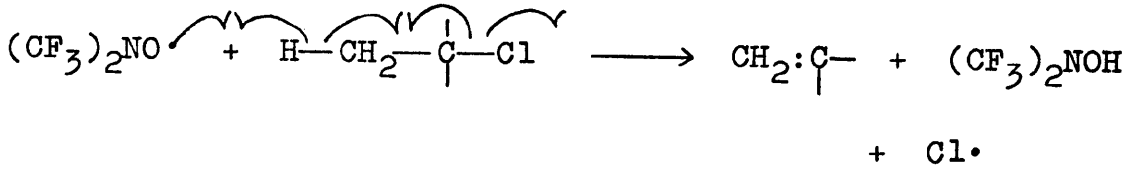
2. Chloroalkanes

In contrast to the reactions of chloroalkenes with the oxyl, those of chloroalkanes result in reasonable yields of products arising from β-scission of chlorine even at room temperature. The initial step in this case involves hydrogen abstraction by the oxyl (and latterly by atomic chlorine liberated *in situ*), to give a primary radical. The energy of activation for abstraction of a primary hydrogen by the oxyl (or chlorine) is considerably higher than that for addition, particularly so in cases where electron-withdrawing groups deactivate the hydrogens towards attack by the electrophilic radicals. As a result, the vicinal chlorine may exert some neighbouring-group effect in the hydrogen abstraction step, an effect not expected in the addition of the oxyl to chloroalkenes. This neighbouring-group participation may occur *via* partial bridging of chlorine, *i.e.*



Although there is some convincing evidence that such bridging may occur in β-bromoalkyl radicals, there is less evidence for bridging by chlorine and any anchimeric assistance to the hydrogen abstraction step would be expected to be considerably less than for that involving bromine.

Alternatively, the hydrogen abstraction step and loss of a chlorine atom could be concerted to some extent, i.e.



It is unlikely that the oxyl would directly couple with the free chlorine atoms due to the low strength of the NO-Cl bond (the oxyl does not react with halogens). However, it is possible that the oxyl interacts with the chlorine to weaken the C-Cl bond and allow β-scission of chlorine to occur.

If loss of chlorine is to some extent concerted with, rather than subsequent to, hydrogen abstraction one would expect to observe rate enhancement in the hydrogen abstraction step. The rates of the reaction of several halogenoalkanes with the oxyl are given in Table 5 (the times given are for the disappearance of oxyl colour).

TABLE 5

Reaction of the oxyl with halogenoalkanes

Halegenoalkane	Temperature	Reaction time
Me_3CBr	ca. 20 °C	30h
Me_3CCl	ca. 20 °C	13d
Me_2CCl_2	ca. 20 °C	440d
$MeCCl_3$	ca. 20 °C then 70-80 °C	not complete after 860d
Me_2CPhCl	ca. 20 °C	35min

For the series of chloroalkanes $MeCX_2Cl$ (where X_2= Me_2; Me,Cl; Cl_2) there is a marked decrease in the reaction rate, due to the increasing number of electron-withdrawing β-chloro substituents which deactivate the primary hydrogens towards the electrophilic oxyl (or chlorine atoms). However, the reaction of 2-chloro-2-phenylpropane with the oxyl was complete in 35min despite the fact both the phenyl group and chlorine are electron-withdrawing substituents. The loss of vicinal chlorine is particularly favourable in this case as it results in a conjugated olefin. If this fragmentation was subsequent to hydrogen abstraction an enhancement in the reaction rate would not be expected.

Similarly, while the considerable difference in the reaction rates of t-butyl bromide and t-butyl chloride may simply be a measure of the different electronegativities of the two halogens, it could also indicate a greater degree

of anchimeric assistance by bromine, either through bridging or more facile β-scission.

(d) The reactions of the oxadiazapentane with halogeno-alkanes

(i) With 2-chloro-2-phenylpropane

The reaction of the oxadiazapentane (7) with a slight excess of 2-chloro-2-phenylpropane at room temperature (5d) gave unchanged oxadiazapentane (7) (ca. 23% recovered), hydrogen chloride (ca. 33% based on consumed alkane), NN-bistrifluoromethylamine (ca. 13% based on consumed oxadiazapentane), NN-bistrifluoromethylhydroxylamine (ca. 39% based on consumed oxadiazapentane), 2-chloro-2-phenylpropane (40% recovered), and a complex mixture of ca. twelve products which could not be separated or identified.

This reaction of the oxadiazapentane (7) is rather more complex than the corresponding reaction of the oxyl (6) as the rate of hydrogen abstraction is initially governed by the rate of fission of the N-O-N bond. Nevertheless, the reaction had not reached completion after five days despite the fact that hydrogen chloride was formed in each case. This indicates that free chlorine competing as a chain-carrier is common to both reactions.

Hence, although, the formation of hydrogen chloride indicates that loss of chlorine from intermediate (21) is again favoured, due to the formation of a conjugated olefin, no rate enhancement was observed. This probably means that loss of chlorine is subsequent to hydrogen abstraction in this case, i.e.

$$(CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2N\cdot + (CF_3)_2NO\cdot$$

$$(CF_3)_2N\cdot + Me_2CPhCl \longrightarrow MeC(Cl)(Ph)CH_2\cdot + (CF_3)_2NH$$

(21)

$$\downarrow$$

$$CH_2{:}CPhMe + Cl\cdot$$

$$Cl\cdot + Me_2CPhCl \longrightarrow (21) + HCl$$

The oxadiazapentane has also been found in the present work to preferentially undergo ring substitution with aryl compounds containing a side chain which is not particularly reactive towards free-radical attack to give NN-bistrifluoromethylhydroxylamine and bistrifluoromethylamino-substituted aromatic compounds, e.g. (see p. 77)

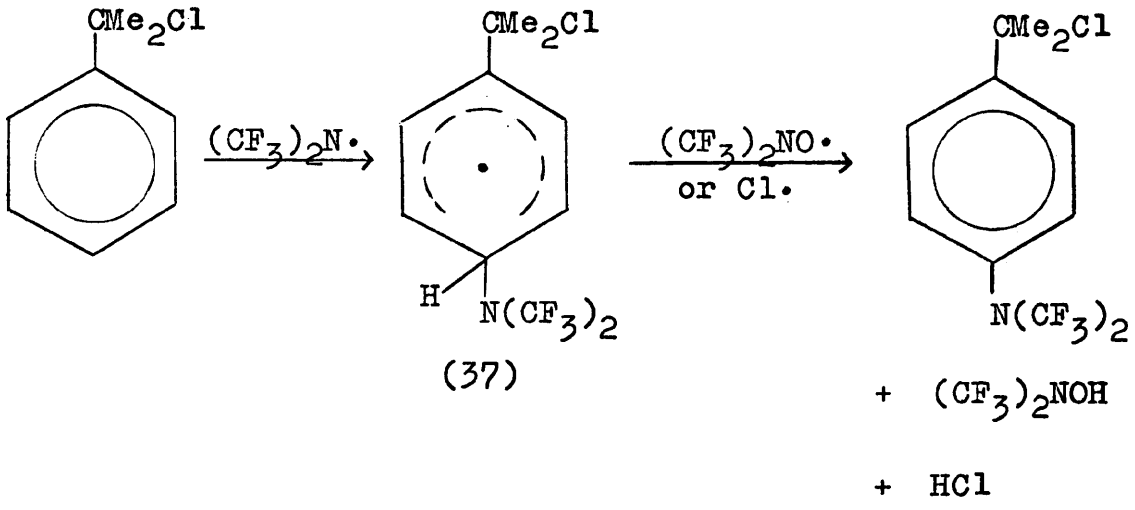
$$Me_3CPh + (7) \longrightarrow Me_3CC_6H_4N(CF_3)_2 + (CF_3)_2NOH$$

(71.5%)

Although a small amount of hydroxylamine is expected in the cumyl chloride reaction as a result of hydrogen abstraction by the oxyl liberated in the initiation step, i.e. fission of the N-O-N bond, the high yield of hydroxylamine (and low yield of NN-bistrifluoromethylamine) indicates that the $(CF_3)_2N\cdot$ radical preferentially attacks the aromatic ring, rather than abstracts a primary hydrogen atom from the

side chain.

The formation of hydrogen chloride in the reaction may be explained by either hydrogen abstraction at the side chain by the free chlorine atoms, or by attack of chlorine on the intermediate cyclohexadienyl radicals (37) formed by attack of the $(CF_3)_2N\cdot$ radical on the aromatic ring, to give hydrogen chloride and bistrifluoromethylamino-substituted derivatives, i.e.

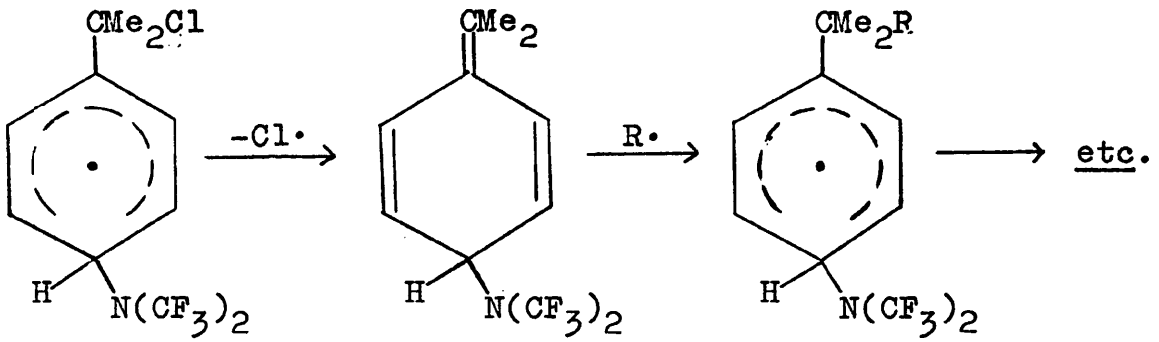


(37)

+ $(CF_3)_2NOH$

+ HCl

The complexity of the reaction may be in part explained by loss of chlorine from intermediate (37) (which may also account for the considerable yield of hydrogen chloride). Intermediate (38) may then undergo further reaction at the CMe_2 group, i.e. (where R·= any radical present in the system)



(37) (38)

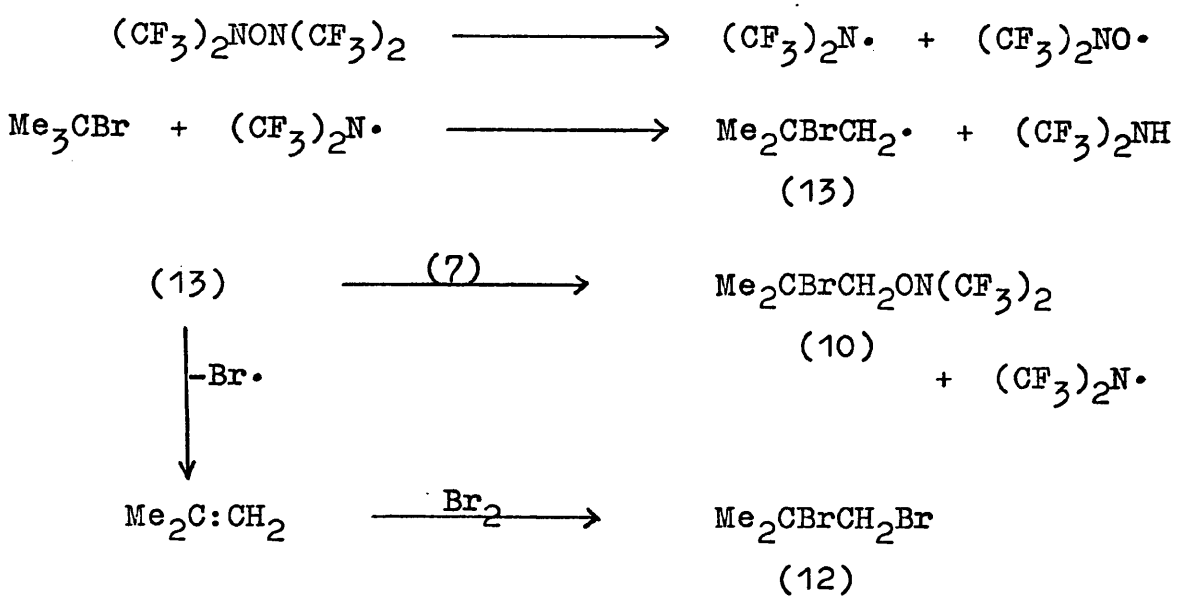
(ii) With t-butyl bromide

An equimolar mixture of the oxadiazapentane (7) and t-butyl bromide on reaction at room temperature (15d) gave NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, a brown liquid (probably bromine), unchanged bromide (ca. 27% recovered), 1,2-dibromo-2-methylpropane (12) (ca. 32% based on consumed bromide), 1-(NN-bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane (10) (ca. 6% based on consumed bromide), and a complex mixture of ca. thirteen unidentified products, which could not be separated.

Products (10) and (12) were identified by g.l.c. analysis, and the lower-boiling products by i.r. spectroscopy. The complexity of the reaction mixture prevented the isolation of the other products.

The formation of the identified products may be explained by the mechanism outlined in Scheme 5. As in the oxyl reaction (p. 36), the formation of the dibromide (12) in reasonable yield indicates that elimination of bromine from the intermediate radical (13) occurred to a considerable extent.

Reaction of the oxadiazapentane (7) with t-butyl bromide



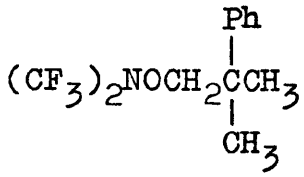
Scheme 5

2. Phenyl migration

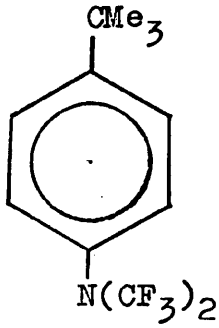
(a) The reactions of the oxyl (6) with arylalkanes

(i) With t-butylbenzene

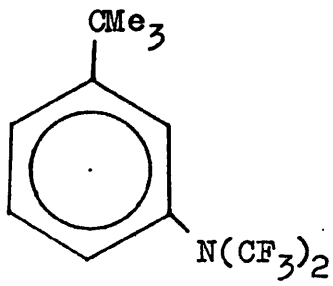
A 3:1 molar mixture of the oxyl and t-butylbenzene on reaction at room temperature (3d) gave NN-bistrifluoromethylhydroxylamine (43% based on oxyl), unchanged t-butylbenzene (21% recovered), 1-(NN-bistrifluoromethylamino-oxy)-2-methyl-2-phenylpropane (39) (28% based on consumed alkane), two minor products tentatively identified as 4-NN-bistrifluoromethylamino-t-butylbenzene (40) (ca. 8% based on consumed alkane) and 3-NN-bistrifluoromethylamino-t-butylbenzene (41) (ca. 6% based on consumed alkane), and some fourteen minor unidentified products which were not present in sufficient quantities to allow their separation and identification.



(39)



(40)



(41)

The amino-oxy product (39) was identified by elemental analysis and the spectroscopic data outlined below. The minor products (40) and (41) could not be isolated pure, and were identified by a comparison of their n.m.r. spectra and g.l.c. retention times with those of known pure samples, (see p. 77).

1-(NN-bistrifluoromethylamino-oxy)-2-methyl-2-phenylpropane (39)

The i.r. spectrum showed absorptions at 3.23-3.45 (C-H str.), and 6.25-6.8 (C:C ring str.) μm, together with bands characteristic of an amino-oxy group.

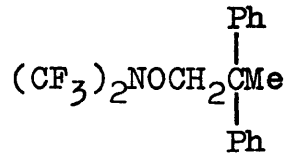
The ^{1}H n.m.r. spectrum showed absorptions at δ 0.94 (6H, s), 3.63 (2H, s), and ca. 6.8 (5H, m) p.p.m., assigned to the two equivalent methyl groups, a $-CH_2ON(CF_3)_2$ group, and the phenyl group, respectively.

The ^{19}F n.m.r. spectrum showed a singlet absorption at δ 41.8 p.p.m. (relative to p-$CF_2ClSC_6H_4Cl$), typical of the fluorines in an amino-oxy group.

The mass spectrum showed peaks at m/e 301 (1%, M^+), 149 (<1%, $C_{10}H_{13}O^+$), 133 (3%, $C_{10}H_{13}^+/C_2F_5N^+$), 119 (21%, $C_9H_{11}^+$), 77 (1.5%, $C_6H_5^+$), and 69 (100%, CF_3^+).

(ii) With 2,2-diphenylpropane

The reaction of a 4:1 molar mixture of the oxyl and 2,2-diphenylpropane at 70-80 °C (3d) gave NN-bistrifluoromethylamine (trace), NN-bistrifluoromethylhydroxylamine (45% based on oxyl), unchanged diphenylpropane (11% recovered), ca. fourteen minor unidentified products, and a compound tentatively identified as 1-(NN-bistrifluoromethylamino-oxy)-2,2-diphenylpropane (42) (36% based on consumed alkane).



(42)

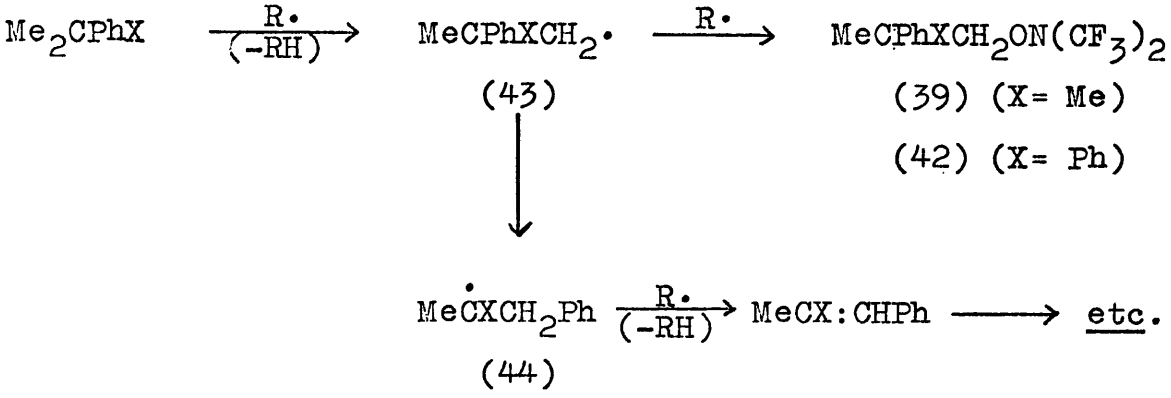
The major product (42) was isolated contaminated with an unidentified amino-oxy-substituted product and was identified on the basis of the n.m.r. spectrum of the two-component mixture. The intractability of the higher-boiling mixture prevented the separation and identification of the minor products.

The ^{1}H n.m.r. spectrum of the major product (42) showed absorptions at δ 1.35 (3H, s), 4.0 (2H, s), and 6.62 (10H, s) p.p.m., assigned to the methyl group, the $-CH_2ON(CF_3)_2$ group, and the phenyl groups, respectively. The ^{19}F n.m.r. spectrum showed a singlet absorption at δ -10.0 p.p.m. (relative to T.F.A.) typical of the fluorines in an amino-oxy group.

Although the reactions of the oxyl with t-butylbenzene and 2,2-diphenylpropane would initially appear simple from

the analytical point of view as hydrogen abstraction by the oxyl gives in both cases a primary radical, the reaction mixtures were very complex, possibly due in part to aromatic ring substitution and/or addition by the oxyl as a result of the low reactivity of the primary side-chain hydrogens.

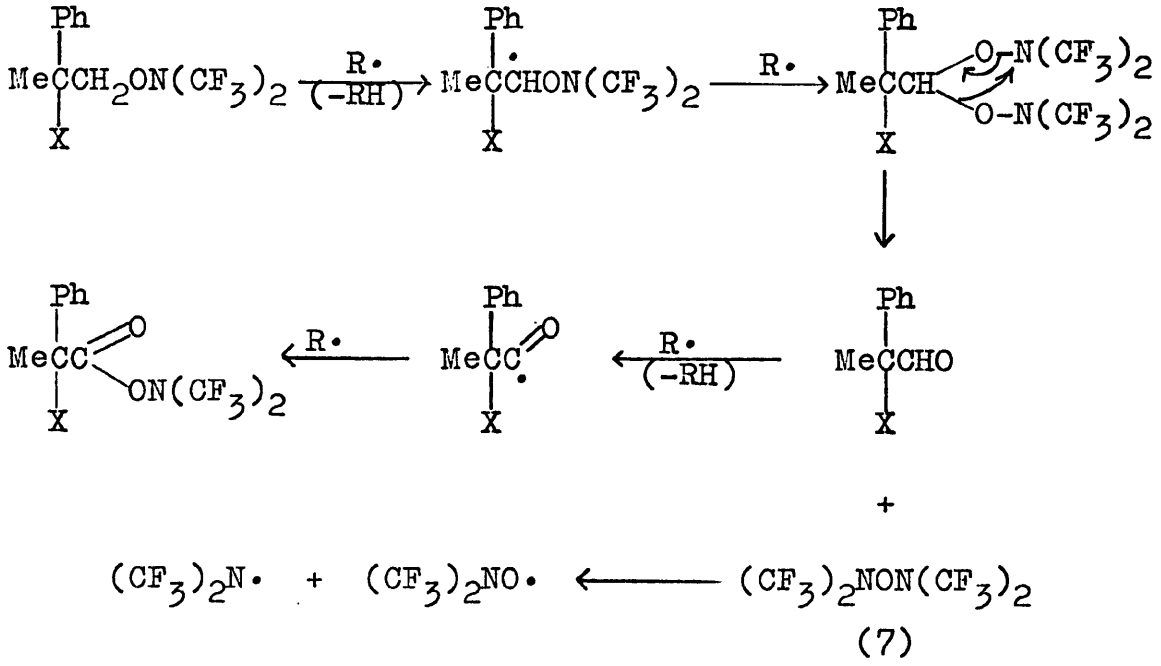
The major products isolated in each reaction were the 1-amino-oxy-substituted derivatives which indicated that the intermediate primary radicals (43) [Scheme 6; where R = $(CF_3)_2NO$, X= Ph or Me] were rapidly scavenged by the oxyl, although it is possible that the rearranged radicals (44) resulting from a 1,2-phenyl shift underwent further reaction with the oxyl to give resonance stabilised olefinic products, i.e.



Scheme 6

The i.r. spectra of the higher-boiling mixtures from both reactions each showed a weak absorption in the region 5.6-6.0 (C:O str.)μm, and since a considerable amount of starting material was recovered in each case, despite using an excess of oxyl, it is considered that further attack of the oxyl at C_1 had occurred to some extent. This further

reaction is believed to involve the steps outlined below [where R = $(CF_3)_2NO$; X= Ph or Me], although several hcmolytic pathways are possible (see p. 30).



$$(CF_3)_2N\cdot + (CF_3)_2NO\cdot \longleftarrow (CF_3)_2NON(CF_3)_2$$

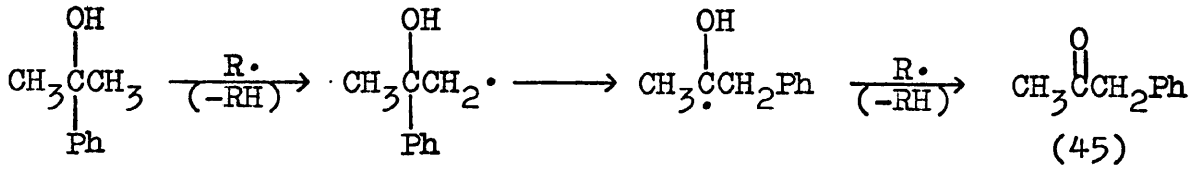
(7)

The bistrifluoromethylamino radicals which are formed can then abstract hydrogen from the side chain to give NN-bistrifluoromethylamine. However, the products formed in the reaction of the oxadiazapentane (7) with t-butylbenzene (p. 77) indicate that the $(CF_3)_2N\cdot$ radical preferentially attacks the aromatic ring, and this then explains the formation of the isolated minor products (40) and (41). The mechanism is discussed further later (see p. 80).

(iii) With 2-phenylpropan-2-ol

The reaction between the oxyl (6) and 2-phenylpropan-2-ol was studied for two reasons; (i) a 1,2-phenyl shift would result in a relatively stable α-hydroxy radical, and (ii) further reaction of the resulting rearranged radical with the

oxyl would give the carbonyl compound (45), via a net oxidation reaction, and so would assist in the identification of rearranged products, i.e.



The reaction of a 2:1 molar mixture of the oxyl and 2-phenylpropan-2-ol at room temperature (3d) gave (i) a volatile fraction, which contained NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, and carbon dioxide, and (ii) an involatile fraction, which contained 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-phenylpropane (20) (ca. 50% based on alcohol), identified by a comparison of its spectroscopic data with that of a pure sample obtained previously (p. 47), several minor unidentified products, three very high-boiling products (A-C) (combined yield ca. 30% based on alcohol), and a small amount of an unidentified solid.

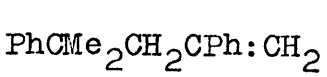
The i.r. spectrum of the higher-boiling mixture did not show any absorptions in the region 5.6-5.9 (C:O str.)μm, indicating that the rearrangement/oxidation had not occurred.

The formation of the major product (20) is difficult to explain in terms of a complete free-radical mechanism, and it was considered that the alcohol may have undergone dehydration. It was also possible that the dehydration was catalysed by the weak acid $(CF_3)_2NOH$, formed in situ, as a result of hydrogen abstraction by the oxyl.

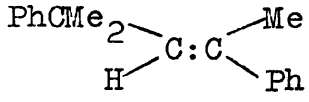
To determine if this were the case, 2-phenylpropan-2-ol

was treated with the hydroxylamine at room temperature (1d) and it was observed that complete dehydration of the alcohol took place.

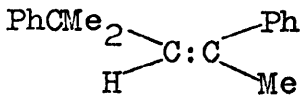
The i.r. spectrum of the higher-boiling mixture, which did not show any absorptions in the region 2.88-3.22 (O-H str.)μm, was typical of that of an aromatic alkene. The mixture was shown by g.l.c. analysis to contain three high-boiling products identical to components A-C obtained in the reaction of the oxyl with the alcohol, and several very minor lower-boiling products. Due to the intractability of the three high-boiling components (A-C) they could not be separated by preparative-scale g.l.c. However, they were tentatively identified as isomeric dimers of α-methylstyrene on the basis of the ^{1}H n.m.r. spectrum of the mixture which showed broad absorptions in the regions δ 0.4-1.4, ca. 1.6-2.5, ca. 4.2-4.8, and ca. 6.7 p.p.m., integrated intensities ca. 12: 3: 1: 17, assigned to the methyl, methylene, olefinic and phenyl groups, respectively, in the three dimers (46), (47), and (48), i.e.



(46)



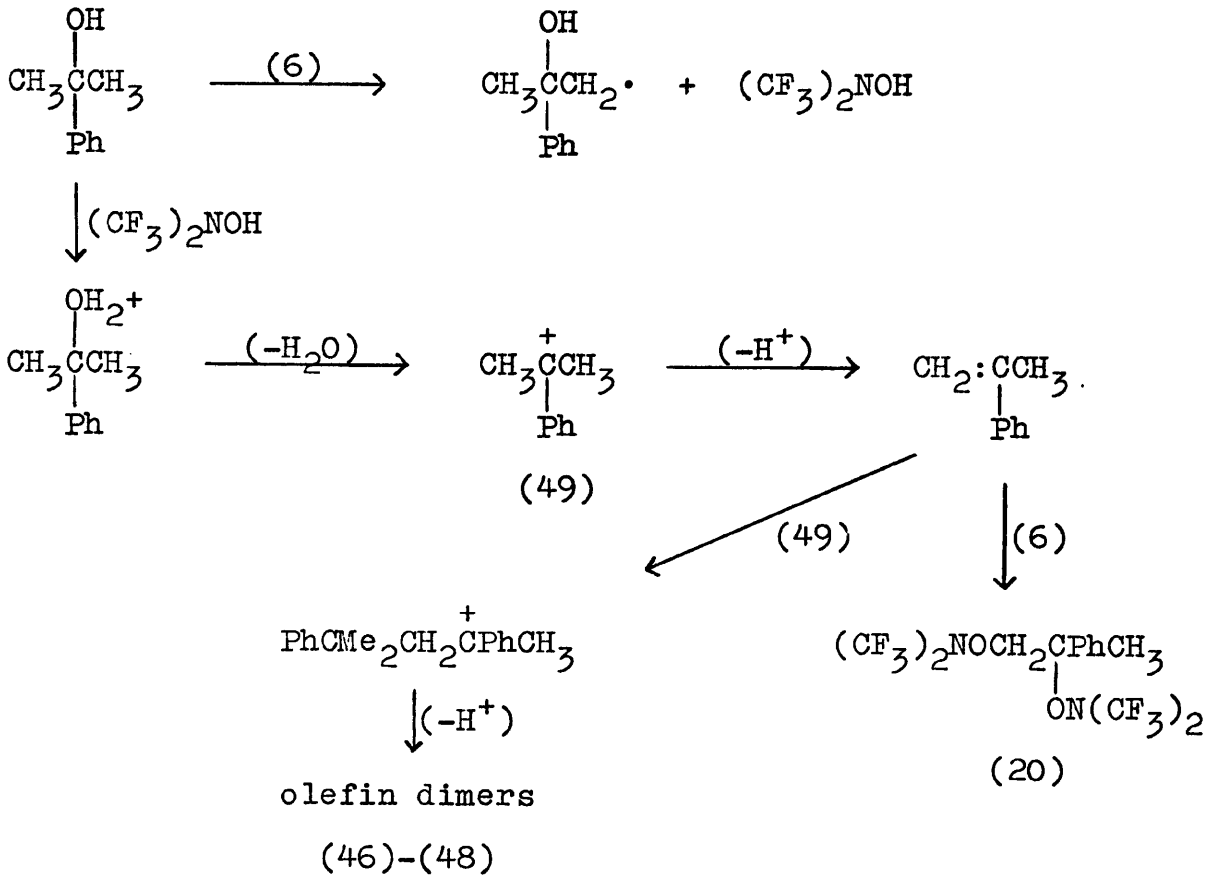
(47)



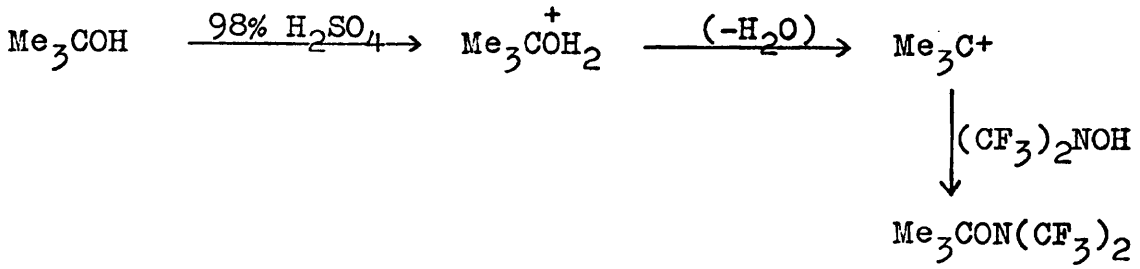
(48)

Confirmation that products (A-C) were olefin dimers was obtained from the mass spectrum of the mixture which showed peaks at m/e 236 (20%, M^+), 221 [67%, $(M-CH_3)^+$], 154 (100%, $C_{12}H_{10}^+$), 143 (22%, $C_{11}H_{11}^+$), 119 (98%, $C_9H_{11}^+$), 91 (53%, $C_7H_7^+$), and 77 (23%, $C_6H_5^+$).

Therefore, in the reaction of the alcohol with the oxyl, the hydroxylamine formed *in situ* as a result of hydrogen abstraction catalyses the dehydration of the alcohol to α-methylstyrene. The olefin may then be scavenged by the oxyl to give the bis(amino-oxy)- adduct (20) or, alternatively, couple with the carbenium ion intermediate (49), with subsequent loss of a proton, to form the isomeric dimers (46)-(48), *i.e.*



Recent work in this department[96] has shown that in the dehydration of certain alcohols catalysed by sulphuric acid, the intermediate carbenium ions may be trapped by the hydroxylamine to give the monosubstituted amino-oxy adducts, *e.g.*



However no amino-oxy absorptions were observed in the i.r. and ^{19}F n.m.r. spectra of the higher-boiling mixture obtained from the reaction between the hydroxylamine and 2-phenylpropan-2-ol. This indicates that direct coupling of the hydroxylamine with intermediate (49) had not occurred in this case.

(b) The reactions of the oxadiazapentane (7) with arylalkanes

(i) With t-butylbenzene

The reaction between an equimolar mixture of the oxadiazapentane (7) and t-butylbenzene at room temperature (7d) gave unchanged oxadiazapentane (12% recovered), NN-bistrifluoromethylamine (9% based on consumed oxadiazapentane), NN-bistrifluoromethylhydroxylamine [47% based on consumed (7)], unchanged t-butylbenzene (36% recovered), several minor unidentified products, 4-NN-bistrifluoromethylamino-t-butylbenzene (40) (40% based on consumed t-butylbenzene), an unidentified NN-bistrifluoromethylamino-t-butylbenzene (A) (31.5% based on consumed alkane), and an unidentified bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)-t-butylcyclohexene (B) (17% based on consumed alkane).

The major product (40) was identified by elemental analysis and spectroscopic data.

The i.r. spectrum showed absorptions at 3.28-3.48 (C-H str.), 6.02-6.84 (C:C ring str.), 7.35-8.66 (C-F str.), 10.22 (C-N str.), 11.92-13.30 (C-H def.), and 13.87 (CF_3 def.)μm.

The ^1H n.m.r. spectrum showed absorptions at δ 0.83 (9H, s) p.p.m., and an AA'BB' type system centred on δ 6.92 (4H) p.p.m., assigned to the nine methyl protons, and the ring protons in a para-subsituted benzene ring, respectively.

A singlet absorption was observed in the ^{19}F n.m.r. spectrum at δ 16.01 (-21.3) p.p.m., typical of the fluorines in a bistrifluoromethylamino group.

The mass spectrum showed peaks at m/e 285 (24%, M^+), 270 [100%, $(M-CH_3)^+$], 266 [9.5%, $(M-F)^+$], 242 [51%, $(M-C_3H_7)^+$], 133 (3%, $C_{10}H_{13}^+/C_2F_5N^+$), 57 (4.5%, $C_4H_9^+$), and 41 (54.5%, $C_3H_5^+$).

Product (A) was identified by elemental analysis and the spectroscopic data outlined below. The n.m.r. spectra of the compound were not sufficiently clear to determine whether it was the ortho- or meta-substituted isomer. The ^1H n.m.r. spectrum showed absorptions at δ 0.83 (9H, s), ca. 6.74 (2H, c), and ca. 7.0 (2H, c) p.p.m., assigned to the nine methyl protons, and the non-equivalent protons in the aromatic ring, respectively.

A singlet absorption was observed in the ^{19}F n.m.r. spectrum at δ 16.01 (-21.3) p.p.m., identical to that of the para-substituted isomer (40), assigned to the fluorines of a bistrifluoromethylamino group.

The mass spectrum showed peaks at m/e 285 (35%, M^+), 270 [100%, $(M-CH_3)^+$], 266 [12%, $(M-F)^+$], 242 [59.5%, $(M-C_3H_7)^+$], 133 (5%, $C_{10}H_{13}^+/C_2F_5N^+$), 69 (13%, CF_3^+), 57 (4%, CMe_3^+), and 41 (58%, $C_3H_5^+$)

Product (B) was identified by elemental analysis and the spectroscopic data outlined below. The microanalysis results were slightly different to the figures required.

The i.r. spectrum showed absorptions at 3.36-3.47 (C-H str.), 7.49-8.55 (C-F str.), 9.59 (C-O-N str.), 10.33 (C-N str.) and 14.08 (CF_3 def.)μm.

The ^1H n.m.r. spectrum showed (i) a singlet absorption at δ 0.97 (9H) p.p.m., assigned to the nine methyl protons, and (ii) poorly resolved, complex absorptions at δ ca. 3.1-3.9 (1H), ca. 4.2-4.6 (1H), ca. 4.6-5.2 (2H), and ca. 5.7-6.4 (1H) p.p.m. The two higher-field signals were assigned to the protons in $>CHN(CF_3)_2$ groups, while the lower-field signals were assigned to the $>CHON(CF_3)_2$ groups, and the olefinic group, respectively.

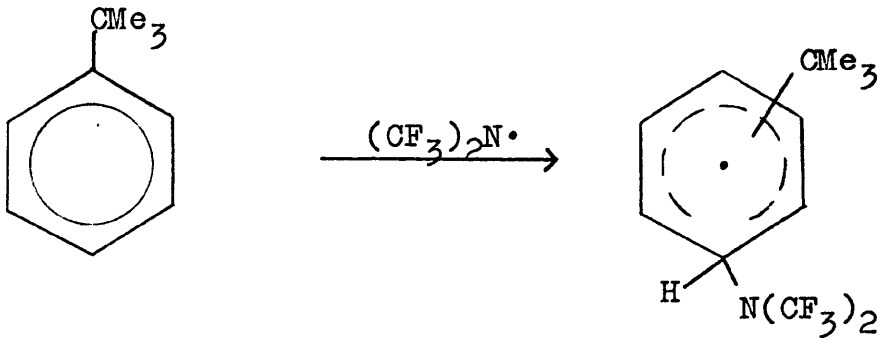
The ^{19}F n.m.r. spectrum showed broad complex absorptions in the regions (i) δ ca. 27.5 (-9.7) to 28.5 (-8.8) p.p.m., and (ii) δ ca. 20.1 (-17.2), ca. 16.3 (-21.0) to 17.7 (-19.5), and ca. 11.2 (-26.1) to 11.9 (-25.4) p.p.m., assigned to the fluorines in (i) the $>CHON(CF_3)_2$ groups, and (ii) the $>CHN(CF_3)_2$ groups, respectively. The complexity of the spectra indicate that the isolated sample was a mixture of several isomers.

The mass spectrum showed peaks at m/e 622 {1%, $[M-(CF_3)_2N]^+$}, 606 {2%, $[M-(CF_3)_2NO]^+$}, 454 (6%, $C_{14}H_{14}F_{12}N_2O^+$), 438 (7.5%, $C_{14}H_{14}F_{12}N_2^+$), 423 (6.5%, $C_{13}H_{11}F_{12}N_2^+$), 318 (3%,

$C_{12}H_{14}F_6NO_2^+$), 302 (2%, $C_{12}H_{14}F_6NO^+$), 286 (5.5%, $C_{12}H_{14}F_6N^+$), 134 (3%, $C_{10}H_{14}^+$), 69 (56%, CF_3^+), and 57 (100%, $C_4H_9^+$).

The isolated products represent a high yield (ca. 89%) and indicate that in contrast to the oxyl (6), the $(CF_3)_2N\cdot$ radical preferentially undergoes addition to the aromatic ring, rather than abstract a hydrogen atom from the side chain, i.e.

$$(CF_3)_2NON(CF_3)_2 \longrightarrow (CF_3)_2N\cdot + (CF_3)_2NO\cdot$$

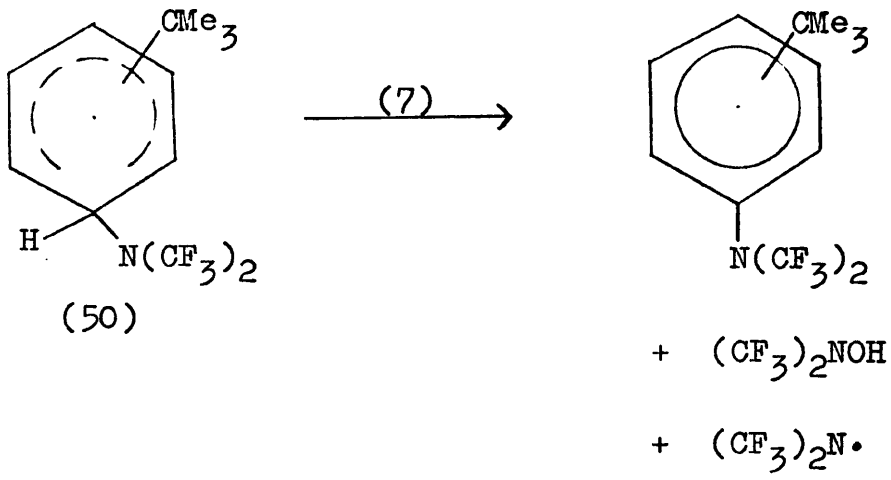


(50)

There are relatively few examples of homolytic aromatic substitution by dialkylamino radicals.[97,98] However, the present work has shown that the electrophilic bistrifluoromethylamino radical readily undergoes addition to olefins (e.g. allylbenzene and penta-1,4-diene) in which an allylic hydrogen is available for abstraction. Therefore it is not surprising that in the reaction with t-butylbenzene, hydrogen abstraction, which would give a primary radical, is not favoured.

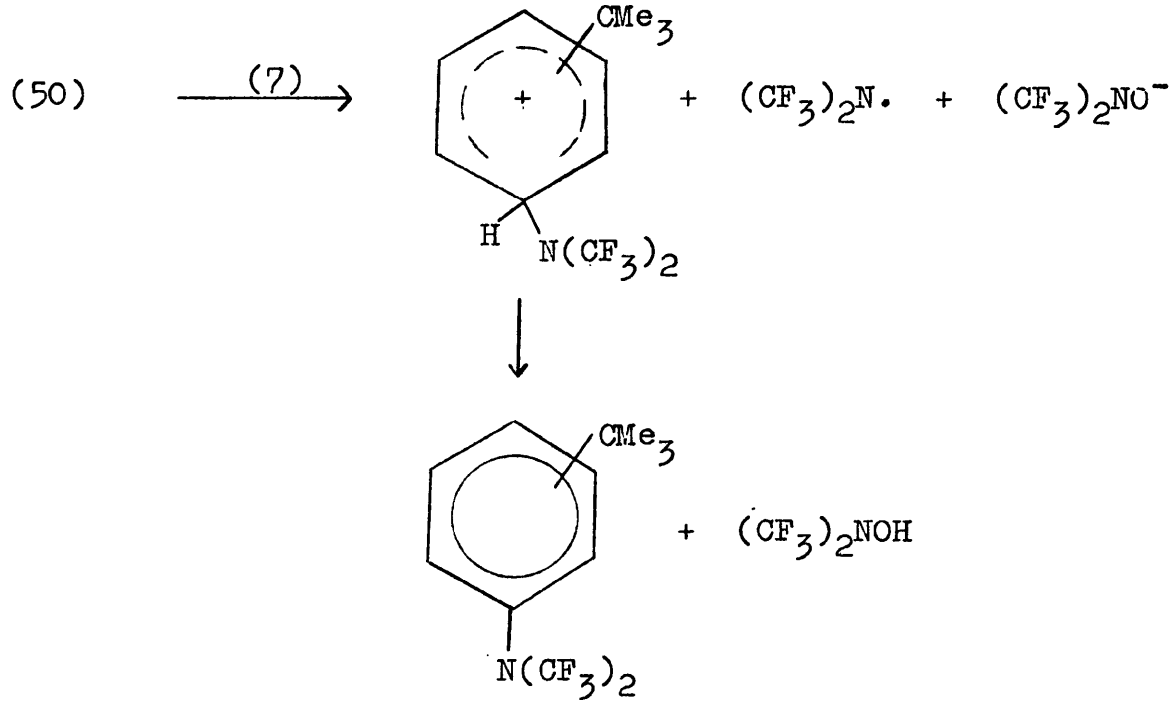
The intermediate cyclohexadienyl radicals (50), formed via addition of the amino radical, may then lose a hydrogen atom to give the bistrifluoromethylamino-t-butylbenzenes (40)

and (A). The oxidation step may occur via reaction of the intermediate cyclohexadienyl radicals with the oxadiazapentane, i.e.

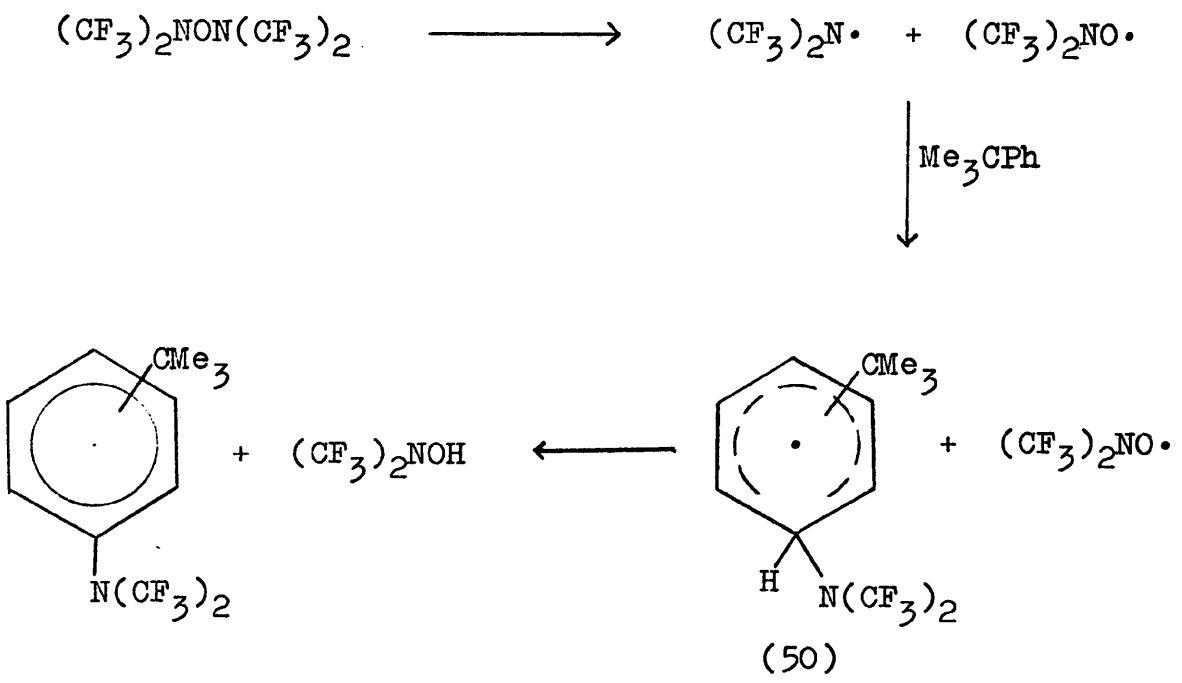


(50)

Although the precise mechanism of the oxidation step is not known, it is possible that some degree of charge transfer is involved in the transition state, e.g.



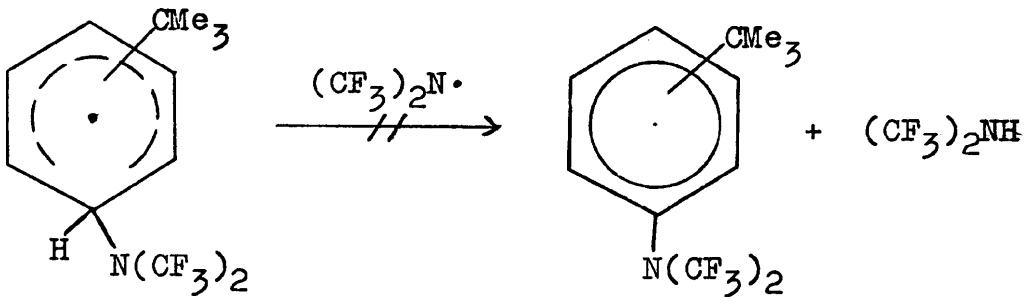
Alternatively, it is possible that on decomposition of the oxadiazapentane, the $(CF_3)_2NO\cdot$ radical does not migrate far from the $(CF_3)_2N\cdot$ radical, and after addition of the latter to the aromatic ring, the $(CF_3)_2NO\cdot$ radical is available to abstract the hydrogen atom from the cyclohexadienyl radical intermediate (50), i.e.



(50)

Products arising from dimerisation or disproportionation of the intermediate cyclohexadienyl radicals were not observed in the reaction products, which perhaps supports the idea of a 'cage' mechanism.

The low yield of NN-bistrifluoromethylamine (ca. 9%) (which may also have been formed via hydrogen abstraction at the side chain) indicates that the reaction of cyclohexadienyl radicals with amino radicals did not occur to any significant extent, i.e.



(50)

Only two amino-substituted t-butylbenzenes were formed in reasonable yield; one was identified as the para-isomer (40), but it was not possible to determine whether the other product (A) was the ortho- or meta-isomer. In general all three isomers are obtained in homolytic aromatic substitution as the transition state involved in the addition step is subject to less electronic distortion than in ionic substitution. With bulky substituents however, (e.g. t-butyl), steric hindrance deactivates the ring towards radical attack, particularly at the normally reactive ortho-position. The extent of deactivation at the ortho- position is dependent on the size and reactivity, and to a lesser extent on the polarity, of the attacking radical. The ratio of isomers obtained in the reaction of t-butylbenzene with several radicals are given in Table 6.

TABLE 6

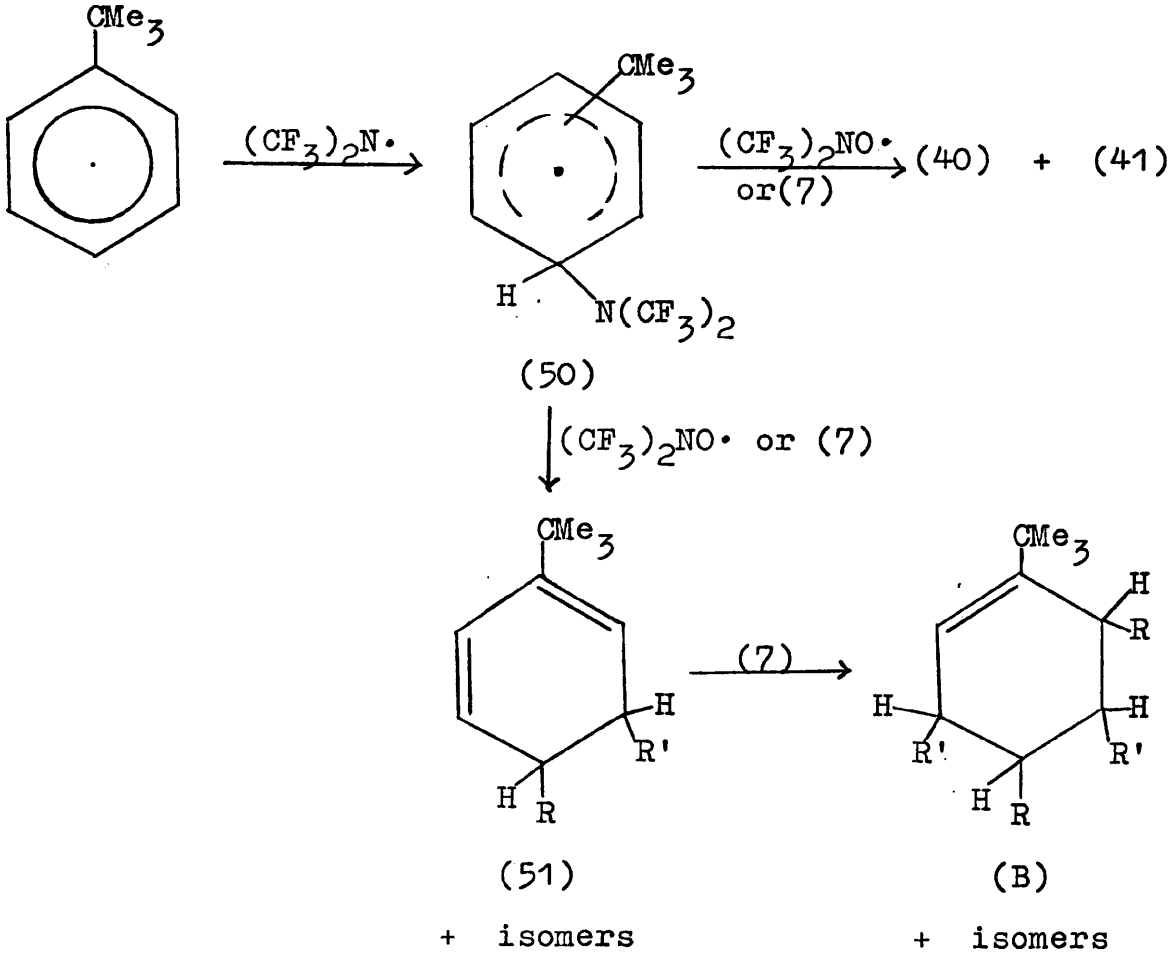
Isomer yields obtained in homolytic substitution of t-butylbenzene

Attacking radical	ortho-(%)	meta-(%)	para-(%)	Reference
c-C_6H_{11}·	0	72	28	99
c-C_3H_5·	2	64	34	100
C_6H_5·	24	49	27	101

It is therefore considered that product (A) is probably the meta-isomer (41), since the transition state involved in the attack of the relatively bulky $(CF_3)_2N$· radical at the ortho- position will be subject to considerable steric interaction.

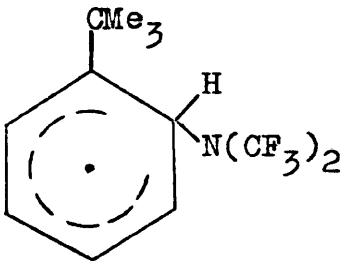
An alternative mechanism by which the intermediate cyclohexadienyl radicals may react is via coupling with the $(CF_3)_2NO$· radicals (or with the oxadiazapentane) to give NN-bistrifluoromethylamino-(NN-bistrifluoromethylamino-oxy)-t-butylcyclohexadienes (51) [Scheme 7; where R= $(CF_3)_2NO$, R'= $(CF_3)_2N$] which may then react further with the oxadiazapentane either via 1,4- or 1,2-addition to form product (B).

Formation of addition product (B) in the reaction of the oxadiazapentane (7) with t-butylbenzene

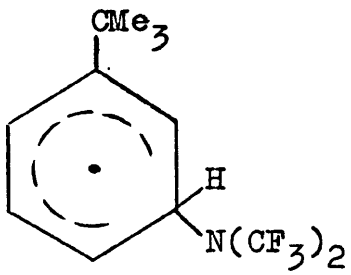


Scheme 7

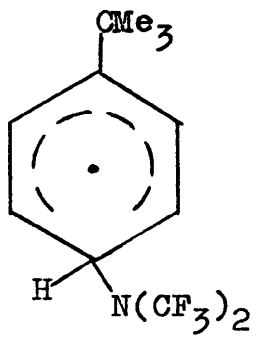
It is improbable that the relative rates of oxidation and coupling of the three possible isomeric cyclohexadienyl radicals (50a, 50b, and 50c) will be the same, because of the presence of the bulky amino- and t-butyl-substituents. As a result, the yields of aromatic isomers obtained are unlikely to reflect accurately the relative rates of initial $(CF_3)_2N\cdot$ radical attack at the ortho-, meta-, and para-positions.



(50a)



(50b)



(50c)

(ii) With 2-phenylpropan-2-ol

The reaction between an equimolar mixture of the oxadiazapentane (7) and 2-phenylpropan-2-ol at room temperature (18d) gave NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine [combined yield ca. 9% based on (7)], and a higher-boiling mixture which contained the three isomeric dimers (A-C) (see p. 75) (combined yield ca. 10% based on alcohol), ca. eleven unidentified liquid products, and an unidentified white solid (trace).

The complexity of the reaction mixture prevented the separation of the higher-boiling products, although the absence of carbonyl absorptions in the i.r. spectrum of the mixture indicated that rearrangement/oxidation had not occurred.

The low yields of lower-boiling products [i.e. $(CF_3)_2NH$ and $(CF_3)_2NOH$] formed in the reaction indicated that hydrogen abstraction at the methyl group, or homolytic aromatic substitution by the $(CF_3)_2N\cdot$ radical had not occurred to any great extent. It is therefore considered that the complexity of the reaction is due, at least in part, to the dehydration of the alcohol in situ as has been

suggested for the corresponding oxyl reaction (p. 73).

(c) The reaction of the oxadiazapentane with chlorobenzene

The reaction of the oxadiazapentane (7) with chlorobenzene was carried out to investigate the extent of homolytic aromatic substitution by the $(CF_3)_2N\cdot$ radical as a route to NN-bistrifluoromethylaminochlorobenzenes of possible synthetic utility.

An equimolar mixture of (7) and chlorobenzene on reaction at room temperature (7d) gave unchanged (7) (19% recovered), hydrogen chloride (8% based on consumed chlorobenzene), NN-bistrifluoromethylamine (7.5% based on consumed oxadiazapentane), NN-bistrifluoromethylhydroxylamine [48% based on consumed (7)], unchanged chlorobenzene (36% recovered), ca. eleven minor unidentified products, a product tentatively identified as an NN-bistrifluoromethylamino-chlorobenzene (A) (ca. 43% based on consumed chlorobenzene), and a product tentatively identified as a bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)chlorocyclohexene (B) (ca. 18% based on consumed chlorobenzene).

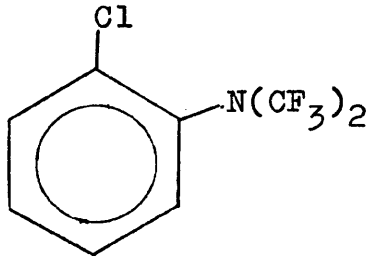
Product (A) was identified by the spectroscopic data outlined below; the microanalysis figures were slightly different from those required and indicated that the isolated sample was slightly impure.

The i.r. spectrum showed absorptions at 3.25-3.32 (C-H str.), 6.08-6.85 (C:C ring str.), 7.43-8.64 (C-F str.), 10.22 (C-N str.), 14.12 (CF_3 def.), and 12.27-14.49 (C-H def.) μm

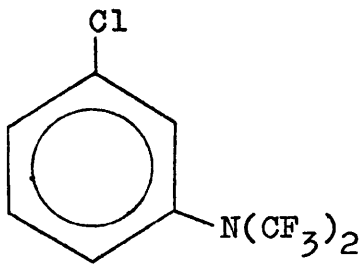
The ^1H n.m.r. spectrum showed a broad singlet at δ 6.9 p.p.m., and it was not possible to tell whether the product

was the ortho- (52) or meta-substituted (53) isomer. Broad complex absorptions were also seen at δ 4.1-4.6 and 5.7-6.0 p.p.m., assigned to the impurity present in the isolated sample. The ^{19}F n.m.r. spectrum showed a singlet absorption at δ 16.75 (-20.5) p.p.m., typical of the fluorines in a bistrifluoromethylamino group.

The mass spectrum showed peaks at m/e 263 (75.5%, M^+), 244 [16%, $(M-F)^+$], 194 [29.5%, $(M-CF_3)^+$], 175 (30%, $C_7H_4ClF_2N^+$), 111 (15%, $C_6H_4Cl^+$), and 69 (100%, CF_3^+).



(52)



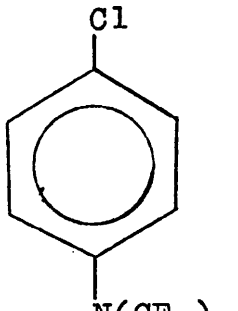
(53)

Product (B) was identified by the spectroscopic data outlined below. The microanalysis figures were slightly different to those required.

The i.r. spectrum showed absorptions at 3.23-3.39 (C-H str.), 6.08-6.83 (C:C ring str.), 7.43-8.65 (C-F str.), 9.61 (C-O-N str.), 10.22-10.35 (C-N str.), 14.10 (CF_3 def.), and 11.24-14.45 (C-H def.)μm.

The ^1H n.m.r. spectrum showed poorly resolved, complex absorptions at δ ca. 3.3-4.9 (4H) and ca. 6.1-6.4 (1H) p.p.m., assigned to the $>CHN(CF_3)_2$ and $>CHON(CF_3)_2$ groups, and the olefinic proton, respectively, together with an AA'BB' type system centred on δ 6.95 p.p.m., typical of the protons in

a para-substituted benzene derivative. It is therefore considered that the isolated sample contained 4-NN-bistrifluoromethylaminochlorobenzene (54) as a contaminant.



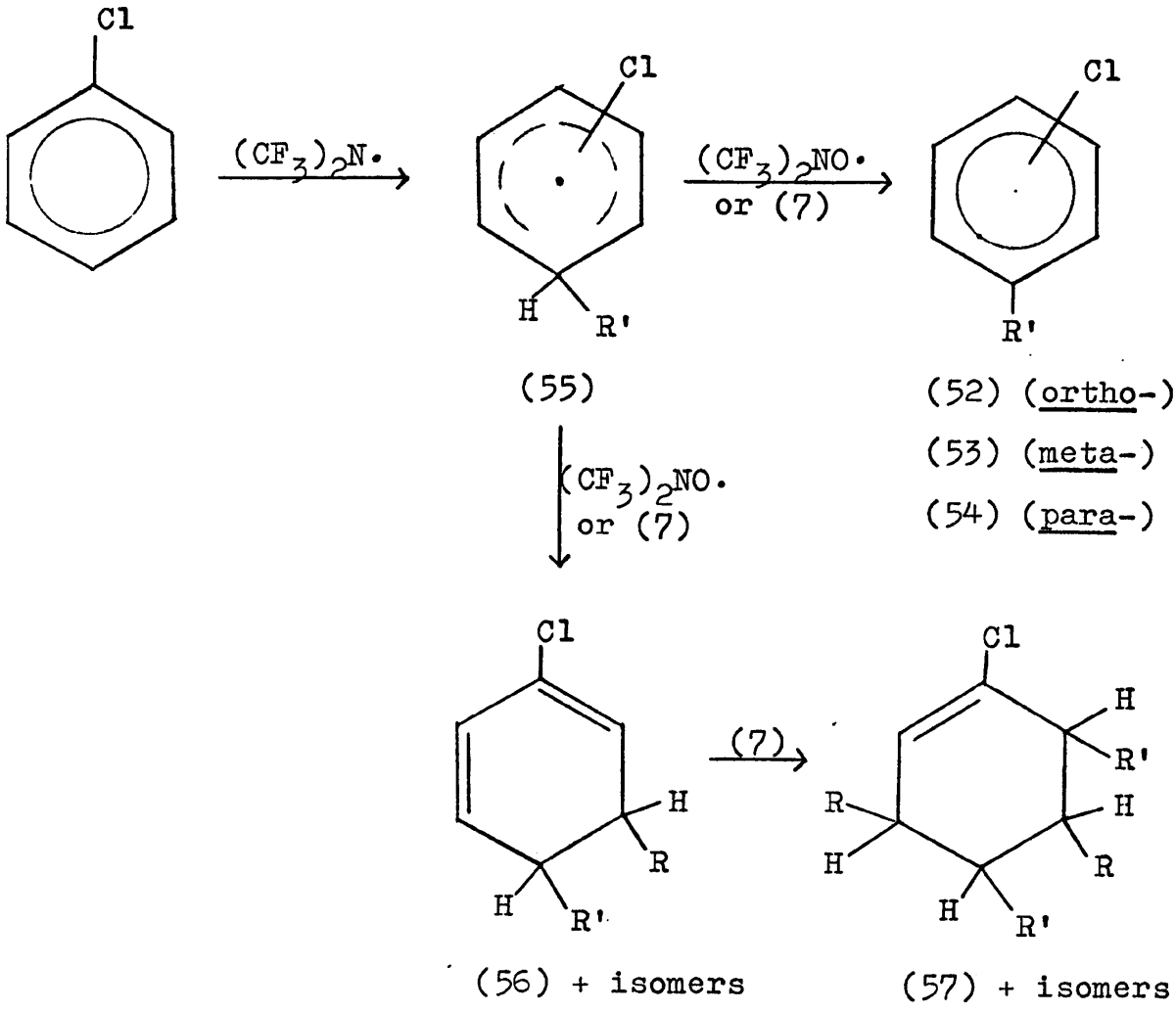
(54)

The ^{19}F n.m.r. spectrum showed absorptions at δ 12.1 (-25.0) (c), 17.35 (-19.9) (s), ca. 29.0 (-8.4) (c), and 29.6 (-7.7) (s) p.p.m., integrated intensities 1: 3: 3: 2.5. It was not possible to determine which absorptions were due to the bis(amino)-bis(amino-oxy)chlorocyclohexene (B) or to the para-substituted derivative (54).

The mass spectrum showed peaks at (i) m/e 600 (1%, $C_{12}H_5ClF_{18}N_3O_2^+$), 584 (2%, $C_{12}H_5ClF_{18}N_3O^+$), 432 (4%, $C_{10}H_5ClF_{12}N_2O^+$), 397 (2.5%, $C_{10}H_5F_{12}N_2O^+$), 381 (1.5%, $C_{10}H_5F_{12}N_2^+$), 296 (1%, $C_8H_5ClF_6NO_2^+$), 280 (11%, $C_8H_5ClF_6NO^+$), 264 (10%, $C_8H_5ClF_6N^+$), and 69 (100%, CF_3^+) assigned to product (B), and (ii) 263 (4%, $C_8H_4ClF_6N^+$), 244 (8%, $C_8H_4ClF_5N^+$), 194 (3%, $C_7H_4ClF_3N^+$), and 111 (5.5%, $C_6H_4Cl^+$), assigned to the para-substituted product (54).

The formation of the products may be explained by the mechanism outlined in Scheme 8; [where R= $(CF_3)_2NO$, R'= $(CF_3)_2N$].

Reaction of the oxadiazapentane (7) with chlorobenzene



Scheme 8

Oxidation of the intermediate cyclohexadienyl radicals (55) may conceivably occur via coupling with the oxyl or via the induced decomposition of the oxadiazapentane (see p. 81).

It was not possible to determine from the ^1H n.m.r. spectrum of the major product (A) whether it was the ortho- (52) or meta-substituted (53) isomer. The ratio of isomers obtained in the reactions of chlorobenzene with various radicals are given in Table 7.

TABLE 7

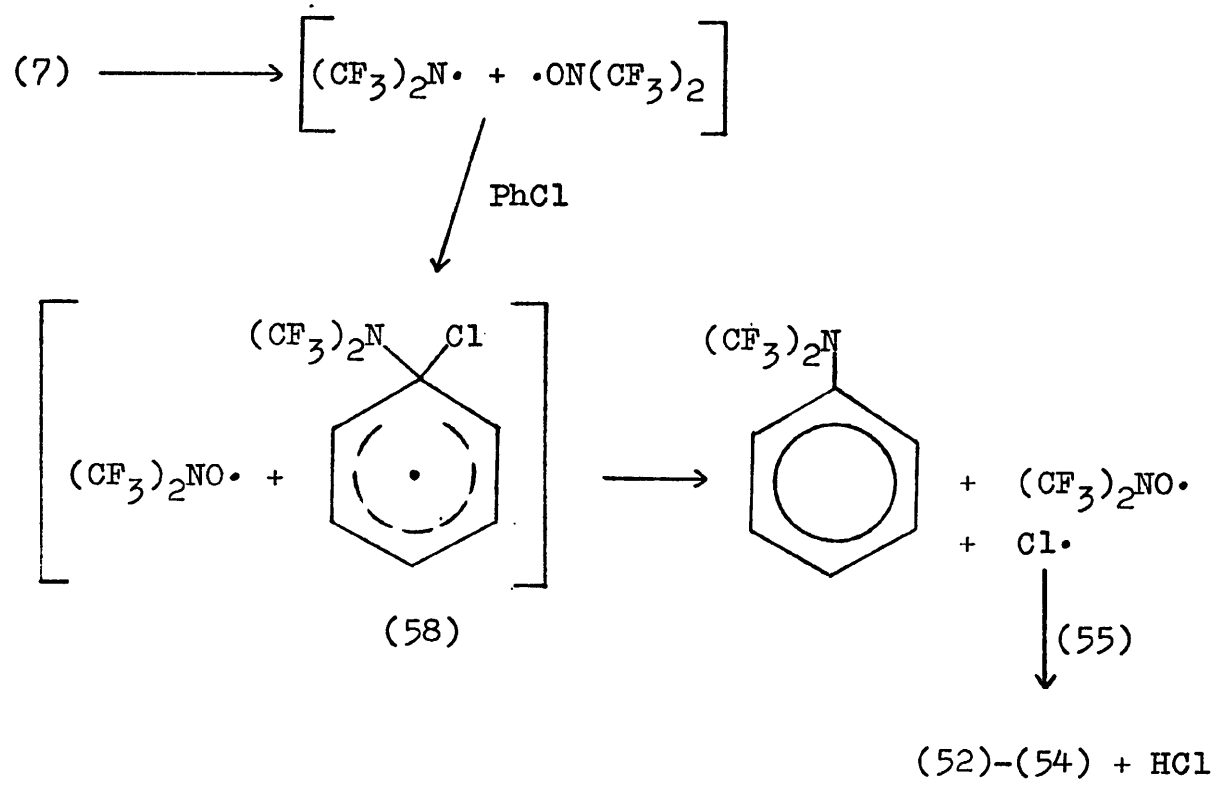
Isomer yields obtained in homolytic substitution of chlorobenzene

Attacking radical	ortho-(%)	meta-(%)	para-(%)	Reference
Ph·	50	32	18	101
c-C_6H_{11}·	54	34	12	99
c-C_3H_5·	59	27	14	100
C_6F_5·	65	21	15	102

Since in all cases the major product is the ortho-isomer, it is probable that the product (A) in the present reaction is also the ortho-isomer (52).

The formation of product (B) indicates that the intermediate cyclohexadienyl radicals (55) can also couple with the oxyl (or the oxadiazapentane), to form the cyclohexadiene (56) which then undergoes further reaction with (7).

The presence of hydrogen chloride in the products may be explained by homolytic substitution of a chlorine atom rather than a hydrogen atom. The fragmentation of the chlorine atom from the intermediate cyclohexadienyl radical (58) may be aided to some extent by the close proximity of the $(CF_3)_2NO$· radical, i.e.



Although it is unlikely that the oxyl (6) would directly couple with the free chlorine atoms (the oxyl does not react with halogens), it is possible that some interaction occurs which aids the fragmentation step (cf. β-scission of chlorine in β-chloroalkyl radicals, p. 62).

The replacement of a halogen rather than a hydrogen atom in homolytic aromatic substitution is rather uncommon, but several examples are known.[103-105] Thus it has been found that in the phenylation of bromo- and chloro-pentafluorobenzene, fluorine was substituted in preference to bromine or chlorine. The same picture emerged from a study of the cyclohexylation of dihalogenobenzenes, from which it was found that the ease of replacement of halogens was in the order; F > I > Br > Cl.[105]

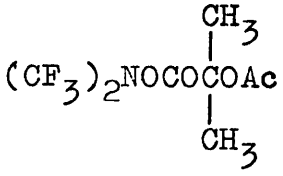
It is apparent therefore that the ease of halogen displacement is not dependent on the strength of the C-X bond

and that displacement of halogen can occur more readily than hydrogen under suitable conditions.

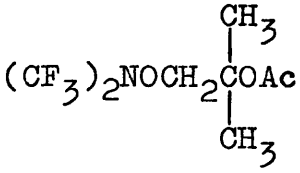
3. Acetyl migration

Reaction of the oxyl (6) with t-butyl acetate

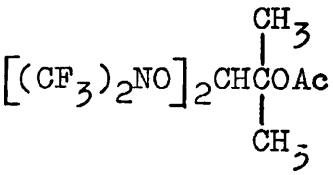
A 2:1 molar mixture of the oxyl (6) and t-butyl acetate on reaction at room temperature (41d) gave NN-bistrifluoromethylamine (ca. 3% based on oxyl), NN-bistrifluoromethylhydroxylamine (49% based on oxyl), unchanged acetate (51% recovered), 1,1-dimethyl-2-(NN-bistrifluoromethylamino-oxy)-2-oxoethyl acetate (59) (40% based on consumed ester), several minor unidentified products, and two products tentatively identified as 1,1-dimethyl-2-(NN-bistrifluoromethylamino-oxy)ethyl acetate (60) (ca. 36% based on consumed ester), and 1,1-dimethyl-2,2-bis(NN-bistrifluoromethylamino-oxy)ethyl acetate (61) (ca. 15% based on consumed ester).



(59)



(60)



(61)

The di-ester (59) was identified by elemental analysis and spectroscopic data. The two other major products (60) and (61) were isolated together and were identified by a consideration of the spectral data obtained for the two-component mixture.

The i.r. spectrum of the di-ester (59) showed absorptions at 3.33-3.45 (C-H str.), 5.47-5.71 (C:O str.), 7.63-8.30 (C-F

str.), 9.44 or 9.59 (C-O-N str.), 10.26 (C-N str.), and 14.03 (CF_3 def.)μm.

The ^1H n.m.r. spectrum showed singlet absorptions at δ 1.29 and 1.69 p.p.m, integrated intensities 2:1, assigned to the $(CH_3)_2C<$ group and the $CH_3C{:}O$ group, respectively. A singlet absorption was observed in the ^{19}F n.m.r. spectrum at δ 28.34 (-8.9) p.p.m., assigned to the fluorines of the amino-oxy group.

Confirmation of the structure was obtained from the mass spectrum which showed peaks at m/e 282 [1%, $(\underline{M}-CH_3)^+$], 238 [1%, $(\underline{M}-CH_3CO_2)^+$], 196 [1%, $(CF_3)_2NOCO^+$], 145 (3%, $C_6H_9O_4^+$), 129 (8%, $C_6H_9O_3^+$), 101 (35%, $C_5H_9O_2^+$), and 59 (39%, $C_2H_3O_2^+$).

The i.r. spectrum of the mixture of products (60) and (61) showed the characteristic absorptions of an amino-oxy group, together with bands at 3.33-3.43 (C-H str.), and 5.62-5.88 (C:O str.)μm.

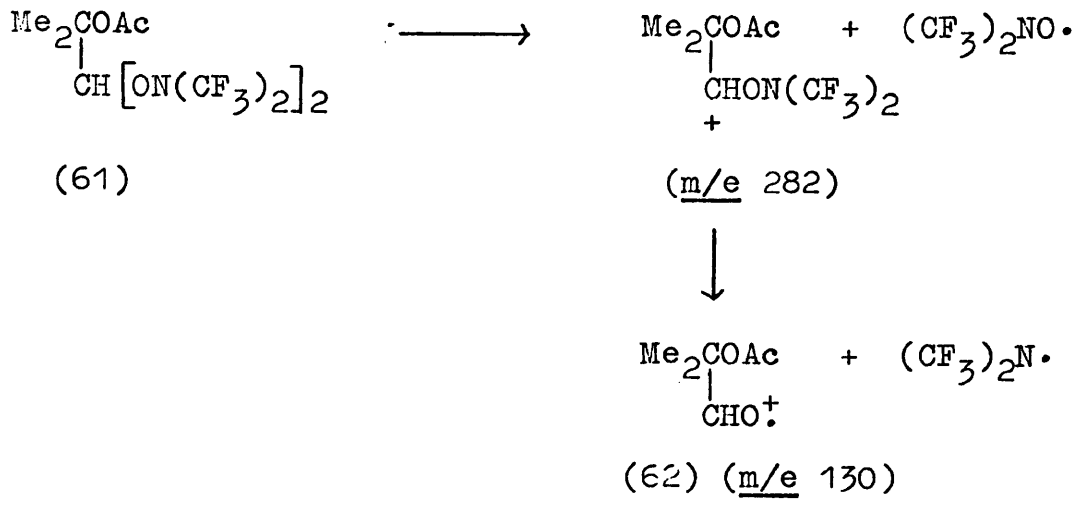
The ^1H n.m.r. spectrum showed absorptions at δ (i) 1.55 (s), assigned to the $(CH_3)_2C$ groups of both compounds, (ii) 1.29 (s) and 3.96 (bs), assigned to the CH_3CO and $-CH_2ON(CF_3)_2$ groups, respectively, in the monosubstituted compound (60), and (iii) at 1.13 (s) and 5.21 (bs) p.p.m., assigned to the CH_3CO and $-CH[ON(CF_3)_2]_2$ groups, respectively, in the disubstituted compound (61).

The ^{19}F n.m.r. spectrum of the mixture showed absorptions at δ 29.7 (-7.6) p.p.m., assigned to the fluorines of the amino-oxy group in the monosubstituted compound (60), and at δ 28.8 (-8.5) p.p.m., assigned to the fluorines of the

equivalent amino-oxy groups in the disubstituted compound (61), (integrated intensities ca. 3:2).

The mass spectrum of the mixture did not provide any conclusive evidence for the disubstituted compound (61), although peaks at m/e 268 [2.5%, $(M-CH_3)^+$], 224 [11%, $(M-OAc)^+$], 115 {5%, $[M-(CF_3)_2NO]^+$}, 101 {34%, $[M-CH_2ON(CF_3)_2]^+$}, 59 (23.5%, OAc^+), and 55 (69%, $C_4H_7^+$) confirm the structure of the monosubstituted compound (60).

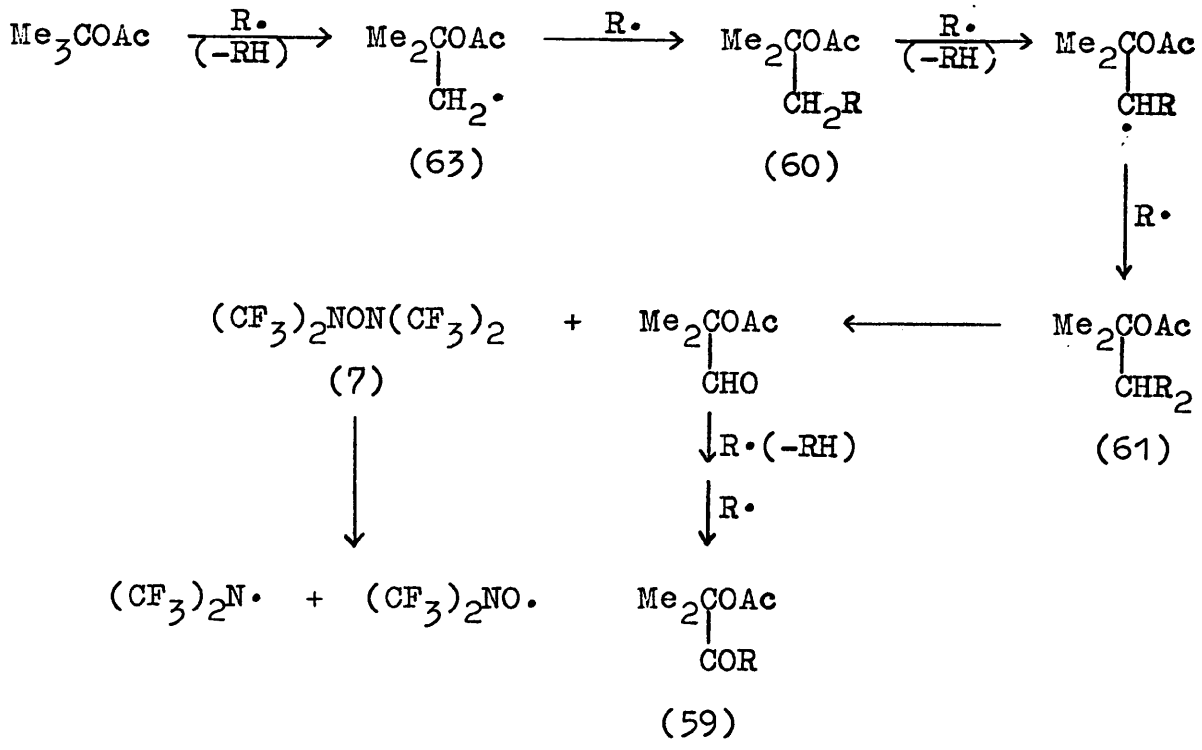
Previous work has shown that the spectra of amino-oxy-substituted compounds rarely show a molecular ion peak, and when it is present it is generally of low intensity. Hence, it is not surprising that the disubstituted compound (61) does not show a molecular ion peak and it is considered that this is due in part to the ease of decomposition of the compound in the mass spectrum, e.g.



The mass spectrum of the mixture showed a peak at m/e 130 (1.5%, $C_6H_{10}O_3^+$) which corresponds to fragment ion (62).

The products may be explained by the mechanism outlined in Scheme 9, [where R= $(CF_3)_2NO$] .

Reaction of the oxyl (6) with t-butyl acetate



Scheme 9

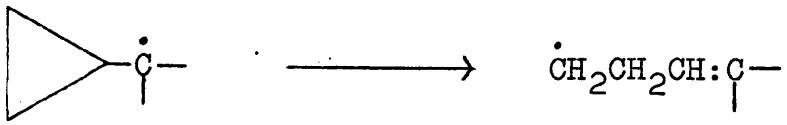
The formation of ester-type products via further attack of the oxyl at an amino-oxy-substituted carbon may be explained by several homolytic pathways (see p. 30). However, the isolation of the disubstituted product (61) in this reaction indicates that the above Scheme is probably involved whereby the bis(amino-oxy) product undergoes decomposition and the resultant aldehyde is then further scavenged by the oxyl to give the di-ester (59).

Products arising from rearrangement or elimination of the acetyl group were not observed and once again this probably reflects the short lifetime of the intermediate radical (63) due to the high concentration of oxyl.

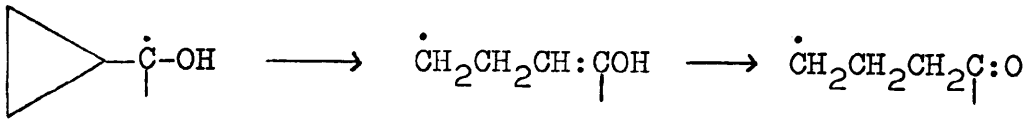
B. Intramolecular fragmentation

1. Cyclopropanes

Although cyclopropane itself does not readily undergo ring opening, cyclopropylcarbinyl radicals have been demonstrated to rearrange to homoallyl radicals under suitable free-radical conditions, i.e.



This fragmentation process was studied in the present work using (a) two cyclopropylcarbinols which may rearrange to cyclic ketones. The rearrangement of α-hydroxyl radicals has been shown to proceed via the enol and does not involve the cleavage of the O-H bond,[106] i.e.



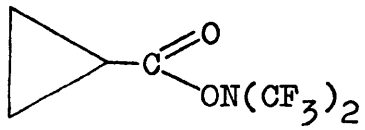
and (b) cyclopropylphenylmethane, in which the ability of the phenyl group to stabilise both the initially-formed cyclopropylcarbinyl radical and the rearranged homoallyl radical, is believed to lower the energy barrier between the two intermediates.

(a) (i) Reaction of the oxyl (6) with cyclopropylcarbinol

The reaction of a 2:1 molar mixture of the oxyl (6) and cyclopropylcarbinol at room temperature (10min) gave NN-bistrifluoromethylhydroxylamine, unchanged alcohol (56% recovered), and one major product (A) (ca. 95% based on

consumed alcohol).

The reaction was then repeated using a 4:1 molar mixture of the oxyl and cyclopropylcarbinol at room temperature (10min) and this gave NN-bistrifluoromethylhydroxylamine (75% based on oxyl), unchanged alcohol (ca. 2.5% recovered), and product (A) (99% based on alcohol), which was identified by elemental analysis and the spectroscopic data outlined below as NN-bistrifluoromethylamino-oxycyclopropane carboxylate (64).



(64)

The i.r. spectrum of compound (64) showed absorptions at 3.23-3.43 (C-H str.), 5.53 (C:O str.), 7.68-8.30 (C-F str.), 9.59 or 9.75 (C-O-N str.), 10.30 (C-N str.), and 14.10 (CF_3 def.)μm.

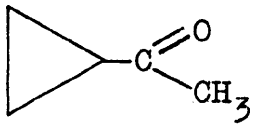
The ^1H n.m.r. spectrum showed absorptions at δ-6.41 (4H, d, J= 6Hz) and-5.76(1H, m) p.p.m. (relative to p-$CCl_2C_6H_4$), assigned to the methylene and methine protons, respectively, in the cyclopropyl ring. The ^{19}F n.m.r. spectrum showed a singlet absorption at δ 29.0 (-8.2) p.p.m., typical of fluorines in an amino-oxy group.

The mass spectrum showed peaks at m/e 218 [1%, $(M-F)^+$], 69 (100%, $CF_3^+/C_4H_5O^+$), 41 (52%, $C_3H_5^+$), and 39 (31.5%, $C_3H_3^+$).

(ii) Reaction of the oxyl (6) with cyclopropylmethylcarbinol

The reaction of a 2:1 molar mixture of the oxyl and cyclopropylmethylcarbinol at room temperature (2min) gave

NN-bistrifluoromethylhydroxylamine (49% based on oxyl), NN-bistrifluoromethylamine (ca. 1.5% based on oxyl), ca. ten minor unidentified products, and cyclopropyl methyl ketone (65) (60% based on alcohol), which was identified by a comparison of its i.r. and n.m.r. spectra with those of an authentic sample. The minor products could not be effectively separated by preparative-scale g.l.c. and were isolated as a mixture, the i.r. spectrum of which showed absorptions in the regions 6.0-6.17 (C:C str.), 2.86-3.23 (O-H str.), and 5.71-5.81 (C:O str.) μm, together with bands typical of an amino-oxy group.

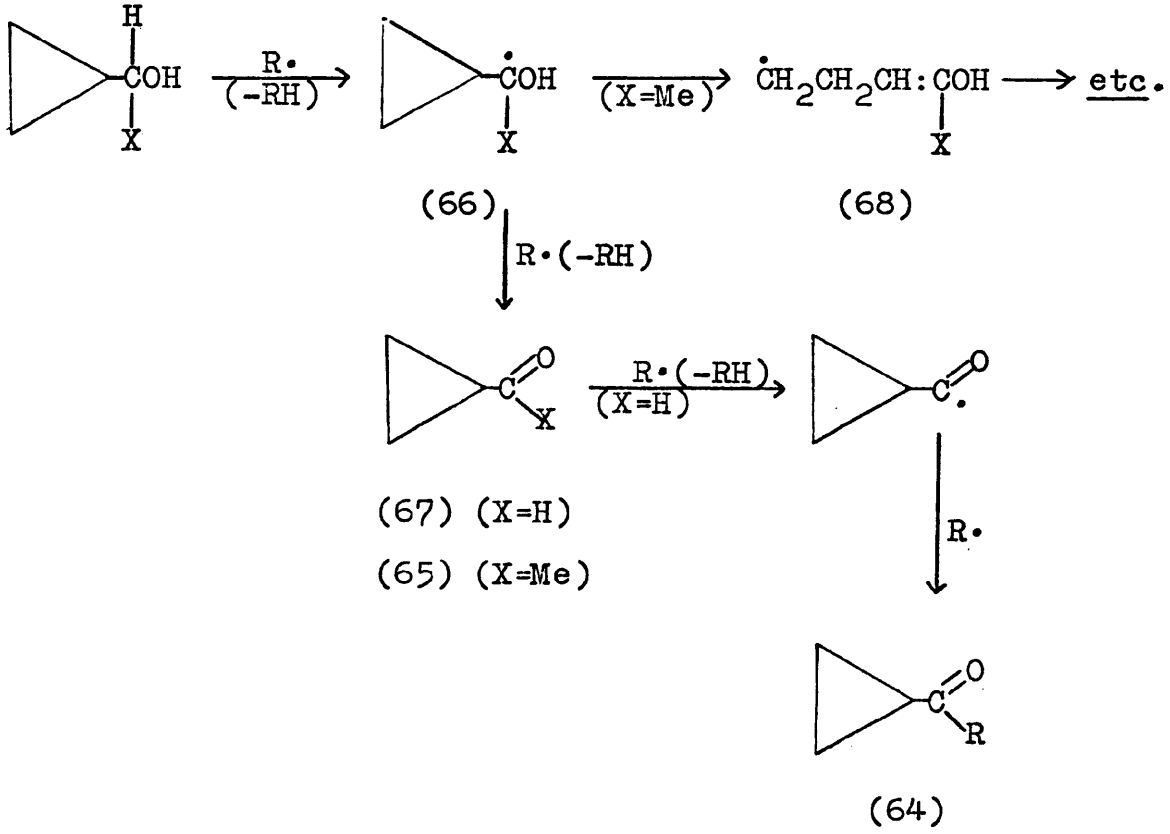


(65)

The formation of the products in each reaction may be explained by the mechanism outlined in Scheme 10 [where R= $(CF_3)_2NO$, X= H or Me].

Hydrogen abstraction by the oxyl (6) gives the α-hydroxy radical intermediate (66) which is then scavenged further by (6) to give the carbonyl products (65) and (67). In the case of cyclopropylcarbinol, the aldehyde (67) reacts further by hydrogen abstraction followed by combination with (6) to give the ester (64).

The faster rate of reaction of (6) with cyclopropylmethylcarbinol compared to cyclopropylcarbinol is probably due to the greater stability of the tertiary radical (66) (X= Me) relative to the secondary radical (66, X= H).



Scheme 10

The extent of oxidation of cyclopropylcarbinols without rearrangement is believed to increase as the stability of the intermediate α-hydroxy radical (66) is increased[106] and therefore it is difficult to explain why the relative yield of carbonyl product is lower with cyclopropylmethylcarbinol than with cyclopropylcarbinol. It is unlikely that attack on the cyclopropyl ring occurs as the reaction of (6) with cyclopropane itself is relatively slow[83]. Furthermore, as the carbons α to the cyclopropyl ring in the starting material may be stabilised by both the cyclopropyl ring and the oxygen of the hydroxy group, it is unlikely that the cyclopropyl methyl ketone formed suffers further hydrogen abstraction by

the oxyl as the relatively acidic hydrogens of the methyl group would not be expected to be particularly reactive towards the electrophilic oxyl radical.

Therefore, it is suggested that the minor unidentified products formed in the reaction of (6) with cyclopropylmethylcarbinol arise *via* ring opening of the intermediate radical (66)(X= Me). Coupling of (6) with intermediate (66) (X= Me) would be expected to be more sterically hindered and hence slower than coupling with intermediate (66) (X= H), thus allowing ring opening to compete with the coupling reaction.

(iii) *Reaction of the oxadiazapentane (7) with cyclopropylcarbinol*

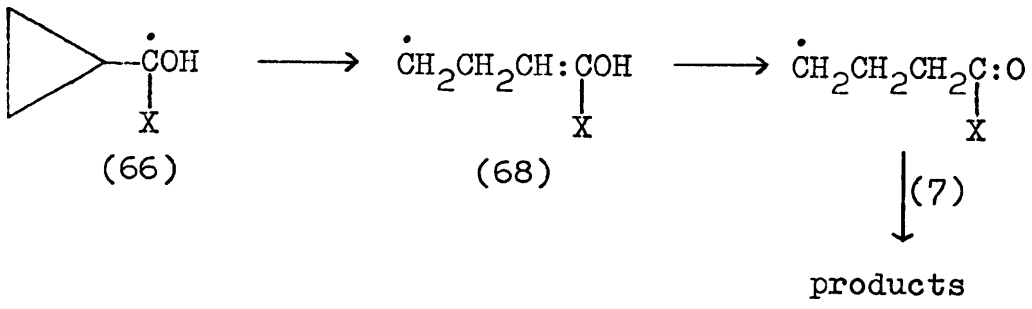
The reaction between an equimolar mixture of (7) and cyclopropylcarbinol at room temperature (18d) gave *NN*-bistrifluoromethylamine (*ca.* 73% based on oxadiazapentane), *NN*-bistrifluoromethylhydroxylamine (yield not determined), and a complex mixture of products which contained *ca.* eight components of relatively short g.l.c. retention times, and *ca.* sixteen components of much longer retention times and which could not be separated. The i.r. spectrum of the mixture showed strong absorptions in the region 5.62-5.95 (C:O str.)μm, together with bands expected for O-H str., C-F str., C-O-N str., and C-N str.

(iv) *Reaction of the oxadiazapentane (7) with cyclopropylmethylcarbinol*

The reaction between an equimolar mixture of (7) and cyclopropylmethylcarbinol at room temperature (7d) gave

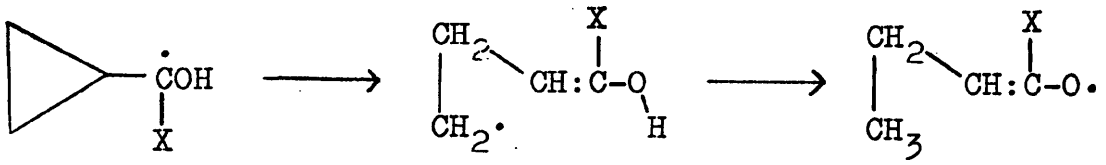
NN-bistrifluoromethylamine (ca. 52% based on oxadiazapentane), NN-bistrifluoromethylhydroxylamine (yield not determined), unchanged alcohol (ca. 18% recovered), and a complex mixture of products which contained ca. eleven components of relatively short g.l.c. retention times, and ca. eleven components of longer retention times and which could not be separated. Once again, the i.r. spectrum of the product mixture showed strong absorptions in the region 5.65-5.95 (C:O str.)μm

The formation of carbonyl products in each reaction indicates that oxidation had taken place as observed in the corresponding oxyl reactions. The complexity of the reaction mixtures formed, however, indicates that ring opening had also occurred to a large extent. The expected enolic radical intermediate (68) then undergoes tautomerisation to the keto- form, i.e. (where X= H or Me)



Due to the slower rate of chain-transfer in the reactions of (7) compared to those involving the oxyl (6), the intermediate (66) has time to undergo rearrangement. Furthermore, recent work involving e.s.r. studies of the intermediates involved in the reactions of cyclopropyl-carbinols has indicated that the enolic radicals formed on

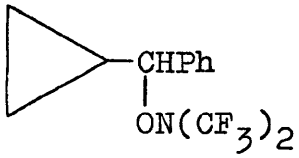
ring opening can undergo a 1,5-shift of the enolic hydrogen to give enoxyl radicals, i.e.[107]



This probably explains, at least in part, the complex mixtures of products formed in these reactions.

(b) (i) Reaction of the oxyl (6) with cyclopropylphenylmethane

The reaction of a 2:1 molar mixture of (6) and cyclopropylphenylmethane at room temperature (10min) gave NN-bistrifluoromethylhydroxylamine (49% based on oxyl), unchanged cyclopropylphenylmethane (9% recovered), several minor unidentified products, and cyclopropyl-(NN-bistrifluoromethylamino-oxy)phenylmethane (69) (95% based on consumed alkane), which was identified by elemental analysis and the spectroscopic data outlined below.



(69)

The reaction was repeated in solution using a 1:2 molar mixture of (6) and cyclopropylphenylmethane in 1,1,2-trichloro-1,2,2-trifluoroethane at room temperature (10min) and this gave NN-bistrifluoromethylhydroxylamine (yield not

determined), unchanged cyclopropylphenylmethane (71.5% recovered), several minor unidentified products, cyclopropyl-(NN-bistrifluoromethylamino-oxy)phenylmethane (69) (84.5% based on consumed alkane), and a previously undetected product (A) (ca. 8% based on consumed alkane) which was not identified.

The i.r. spectrum of compound (69) showed absorptions at 3.27-3.44 (C-H str.), and 6.23-6.70 (C:C ring str.) μm, together with bands typical of an amino-oxy group.

The ^{1}H n.m.r. spectrum showed absorptions at δ (i) ca. -8.2 (4H, c), -7.3 (1H, c), and -4.55 (1H, d, J= 9Hz) p.p.m. (relative to p-$Cl_2C_6H_4$), and (ii) δ 6.87 (5H, c) p.p.m. (relative to TMS), assigned to the methylene and methine protons in the cyclopropyl ring, the proton in a $>CHON(CF_3)_2$ group, and the aromatic ring protons, respectively.

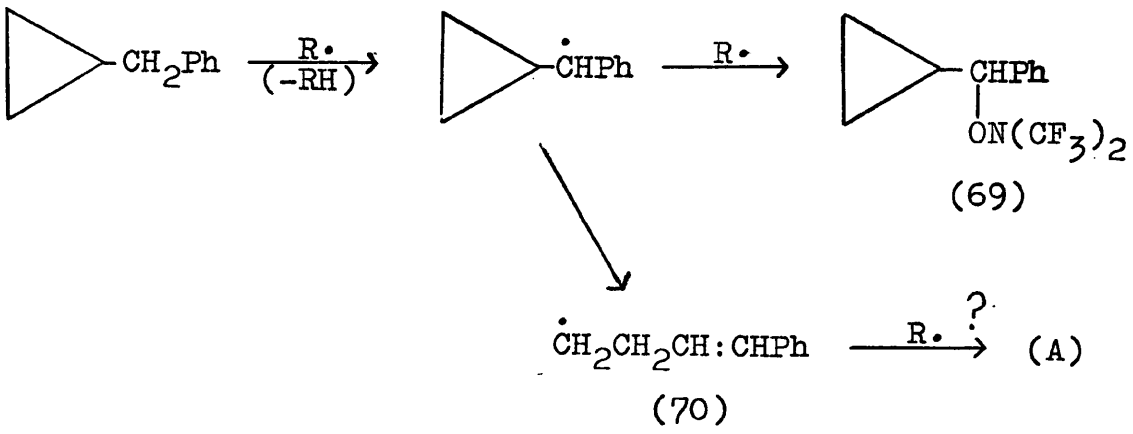
The ^{19}F n.m.r. spectrum showed a broad absorption at δ 27.8 (-9.5) p.p.m., typical of the fluorines in an amino-oxy group bonded to an asymmetric carbon.

The mass spectrum showed peaks at m/e 298 [1%, $(M-H)^+$], 257 (1%, $C_9H_5F_6NO^+$), 131 (100%, $C_{10}H_{11}^+$), 91 (51%, $C_7H_7^+$), 77 (15%, $C_6H_5^+$), and 41 (5%, $C_3H_5^+$).

The formation of the products may be explained by the mechanism outlined in Scheme 11 [where R= $(CF_3)_2NO$].

Although the minor product (A) was not identified, the lower concentration of (6) used in the second reaction would be expected to favour ring opening.

Reaction of the oxyl (6) with cyclopropylphenylmethane



Scheme 11

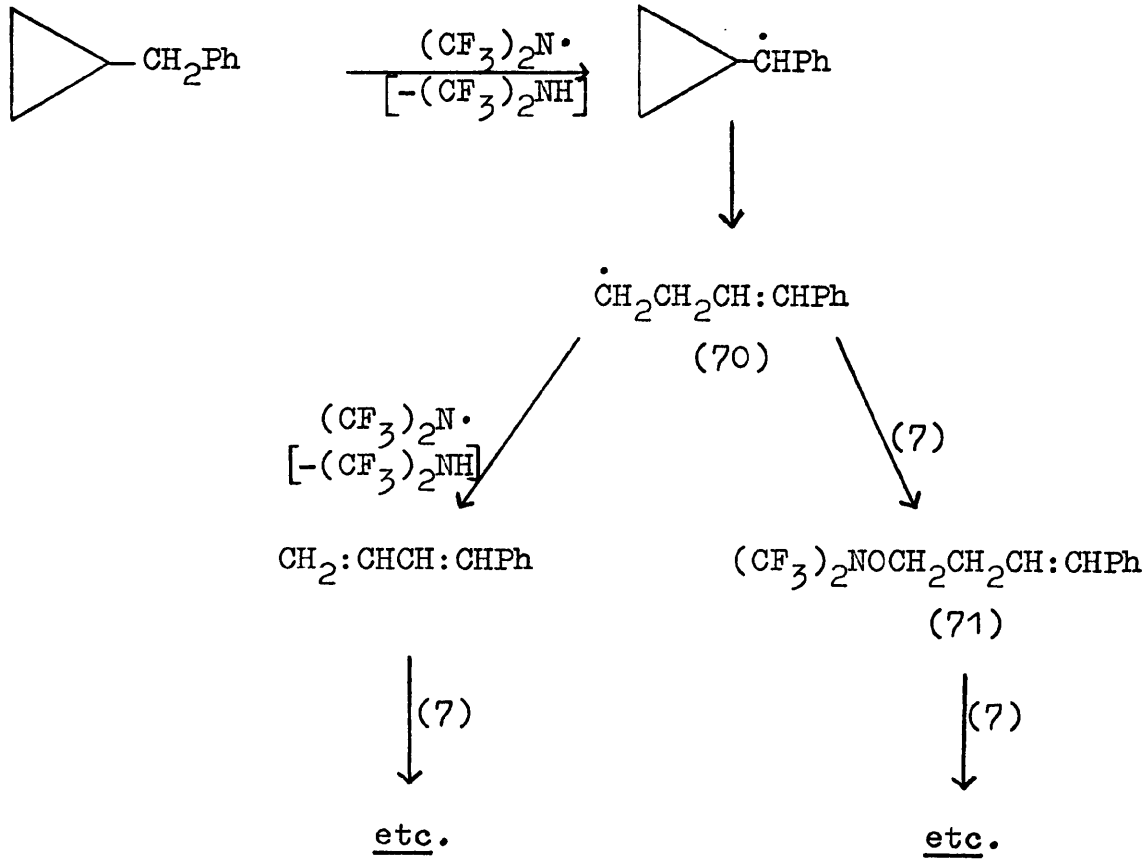
(ii) Reaction of the oxadiazapentane (7) with cyclopropylphenylmethane

The reaction of an equimolar mixture of (7) and cyclopropylphenylmethane at room temperature (1d) gave unchanged (7) (53% recovered), NN-bistrifluoromethylamine [25% based on consumed (7)], NN-bistrifluoromethylhydroxylamine (trace), unchanged cyclopropylphenylmethane (48% recovered), and a complex mixture of ca. nineteen products which could not be separated or identified.

The products were investigated by coupled g.l.c./mass spectrometry but the results were rather ambiguous and it was difficult to assign structures. Several components showed base peaks at m/e 91, with a parent ion at m/e 283, and on this evidence they have been tentatively identified as NN-bistrifluoromethylamino-substituted cyclopropanes of general formula $PhCH_2C_3H_4N(CF_3)_2$.

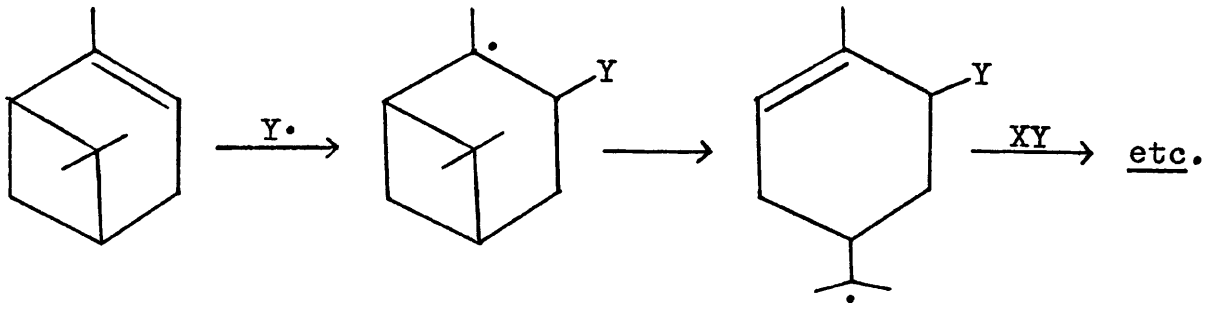
The low yield of NN-bistrifluoromethylhydroxylamine indicates that little, if any, aromatic ring substitution by the $(CF_3)_2N\cdot$ radical had occurred, probably due to the high reactivity of the benzylic hydrogens towards abstraction.

The relatively low yield of NN-bistrifluoromethylamine and the complexity of the reaction products may be explained by further reaction of the ring-opened intermediate (70) and the expected initial product from ring opening, 1-phenyl-4-(NN-bistrifluoromethylamino-oxy)but-1-ene (71), with the oxadiazapentane (7), i.e.



2. Pinenes

Under suitable conditions both 2- and 2(10)-pinene may undergo ring opening due to the inherent strain in the four-membered ring, e.g.



The mode of ring opening in free-radical reactions is confined to the above process which results in the relief of ring strain and the formation of a tertiary radical since radical rearrangements are in general less favourable than those of corresponding carbenium ions.

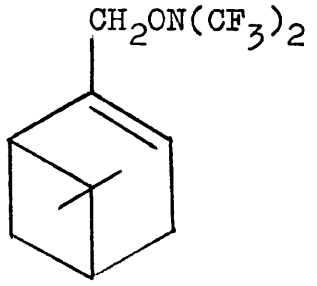
With suitable reagents (e.g. NBS or t-BuOCl) both 2- and 2(10)-pinene have been shown to undergo allylic hydrogen abstraction[69,108-110] and thus it was considered that their reaction with the oxyl (6) would possibly provide evidence for both ring opening and allylic migration.

As a comparison, the reactions of 2- and 2(10)-pinene with the oxadiazapentane (7) were also investigated, although in less detail than for (6). The chain-transfer step in such additions is believed to involve fission of the >N-O-N< bond and being relatively slow should facilitate the fragmentation with respect to that in oxyl reactions.

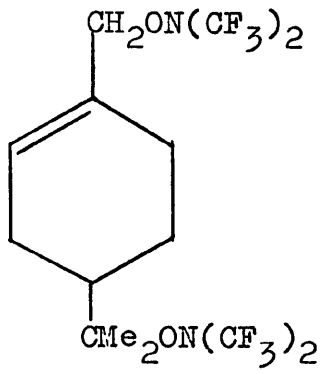
(a) The reactions of the oxyl (6) with pinenes

(i) With 2-(10)-pinene

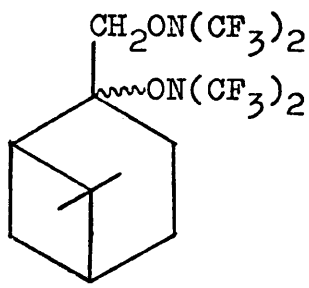
The reaction of a 2:1 molar mixture of (6) and 2(10)-pinene reached completion on warming from -196 °C to room temperature and gave NN-bistrifluoromethylhydroxylamine (26% based on oxyl), unchanged 2(10)-pinene (19% recovered), 10-(NN-bistrifluoromethylamino-oxy)-2-pinene (72) (48% based on consumed pinene), 1-(NN-bistrifluoromethylamino-oxy)-methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclo-hex-1-ene (73) (10% based on consumed pinene), and two disubstituted pinanes (A) (16.5%) and (B) (24% based on consumed pinene), which were identified as diastereoisomers of 2,10-bis(NN-bistrifluoromethylamino-oxy)pinane (74).



(72)



(73)



(74)

To observe the effect of dilution on the product ratio, the reaction was repeated, again using a 2:1 molar mixture, with slow passage of the oxyl through a solution of 2(10)-pinene in 1,1,2-trichloro-1,2,2-trifluoroethane. This gave unchanged pinene (11.5% recovered), (72) (64%), 73 (7%), and (A) (11.5%) and (B) (17.5%).

Thus, while the yield of monosubstituted product (72)

increased, the three disubstituted products (73): (A): (B) were present in almost the same ratio as in the neat reaction. Surprisingly, the yield of rearranged product (73) was not increased on dilution.

The isolated amino-oxy derivatives were identified by elemental analysis and the spectroscopic data outlined below. The microanalysis figures for the rearranged product (73) were slightly different to those required and indicated that the isolated sample was slightly impure.

10-(NN-bistrifluoromethylamino-oxy)-2-pinene (72)

The i.r. spectrum showed the characteristic bands of an amino-oxy group together with absorptions at 3.29-3.52 (C-H str.), and 6.04 (C:C str.)μm.

The ^1H n.m.r. spectrum showed absorptions at δ 0.62 (3H, s), 1.08 (3H, s), 1.37-2.32 (6H, c), 4.11 (2H, s), and 5.37 (1H, m) p.p.m., assigned to the two methyl groups, the six ring protons, the methylene protons in the $-CH_2ON(CF_3)_2$ group, and the olefinic proton, respectively.

The ^{19}F n.m.r. spectrum showed a singlet absorption at δ 41.7 p.p.m. (relative to p-$CF_2ClSC_6H_4Cl$) assigned to the fluorines in an amino-oxy group.

The mass spectrum showed peaks at m/e 303 (3%, M^+), 288 [1%, $(M-CH_3)^+$], 182 [1%, $(CF_3)_2NOCH_2^+$], 135 (37%, $C_{10}H_{15}^+$), and 91 (100%, $C_7H_7^+$).

1-(NN-bistrifluoromethylamino-oxy)methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene (73)

The i.r. spectrum showed the characteristic bands of an amino-oxy group together with absorptions at 3.33-3.45 (C-H

str.), and 5.91 and 6.02 (C:C str.)μm.

The ^{1}H n.m.r. spectrum showed absorptions at δ 0.63 (3H, s), 1.15 (3H, bs), ca. 1.4-2.4 (7H, c), 4.20 (2H, s), and ca. 5.5 (1H, m) p.p.m., assigned to the two methyl groups, the seven ring protons, the methylene protons in the $-CH_2ON(CF_3)_2$ group, and the olefinic proton, respectively.

The ^{19}F n.m.r. spectrum showed absorptions at δ 42.2 (s) and 41.4 (bs) p.p.m. (relative to p-$CF_2ClSC_6H_4Cl$), integrated intensities 1:1, assigned to the fluorines in the $-CH_2ON(CF_3)_2$ and $(CF_3)_2NOCMe_2$ groups, respectively.

The mass spectrum showed peaks at m/e 471 [1%, $(M-H)^+$], 304 {1%, $[M-(CF_3)_2NO]^+$}, 290 {2%, $[M-(CF_3)_2NOCH_2]^+$}, 262 {1%, $[M-(CF_3)_2NOCMe_2]^+$}, 210 [8%, $(CF_3)_2NOCMe_2^+$], 136 (3%, $C_{10}H_{16}^+$), and 69 (100%, CF_3^+).

Diastereoisomer (A)

The i.r. spectrum showed only that it was an amino-oxy-substituted alkane.

The ^{1}H n.m.r. spectrum showed absorptions at δ 0.91 (3H, s), 1.05 (3H, s), 1.24-2.40 (8H, c), and 4.09 (2H, m) p.p.m., assigned to the two methyl groups, the eight ring protons, and the methylene protons in the $-CH_2ON(CF_3)_2$ group, respectively.

The ^{19}F n.m.r. spectrum showed absorptions at δ 42.2 (s) and 4 0.5 (c) p.p.m. (relative to p-$CF_2ClSC_6H_4Cl$), integrated intensities 1:1, assigned to the $(CF_3)_2NOCH_2$ group, and the sterically hindered $>CON(CF_3)_2$ group, respectively

The mass spectrum showed peaks at m/e 472 (1%, M^+), 471 [1.5%, $(M-H)^+$], 304 {23%, $[M-(CF_3)_2NO]^+$}, 182 [1.5%,

$(CF_3)_2NOCH_2^+]$, 136 (36%, $C_{10}H_{16}^+$), and 69 (100%, CF_3^+).

Diastereoisomer (B)

The i.r. spectrum showed only that it was an amino-oxy substituted alkane.

The ^1H n.m.r. spectrum showed absorptions at δ 0.84 (3H, s), 1.13 (3H, s), ca. 1.22-2.25 (8H, c), and 4.05 (2H, m) p.p.m., assigned to the two methyl groups, the eight ring protons, and the $-CH_2ON(CF_3)_2$ group, respectively. The ^{19}F n.m.r. spectrum showed absorptions at δ 28.32 (-8.5) (s) and ca. 27.0 (-10.3) (c) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $(CF_3)_2NOCH_2$ group, and the sterically hindered $-\dot{C}ON(CF_3)_2$ group, respectively.

The mass spectrum was virtually identical to that of diastereoisomer (A).

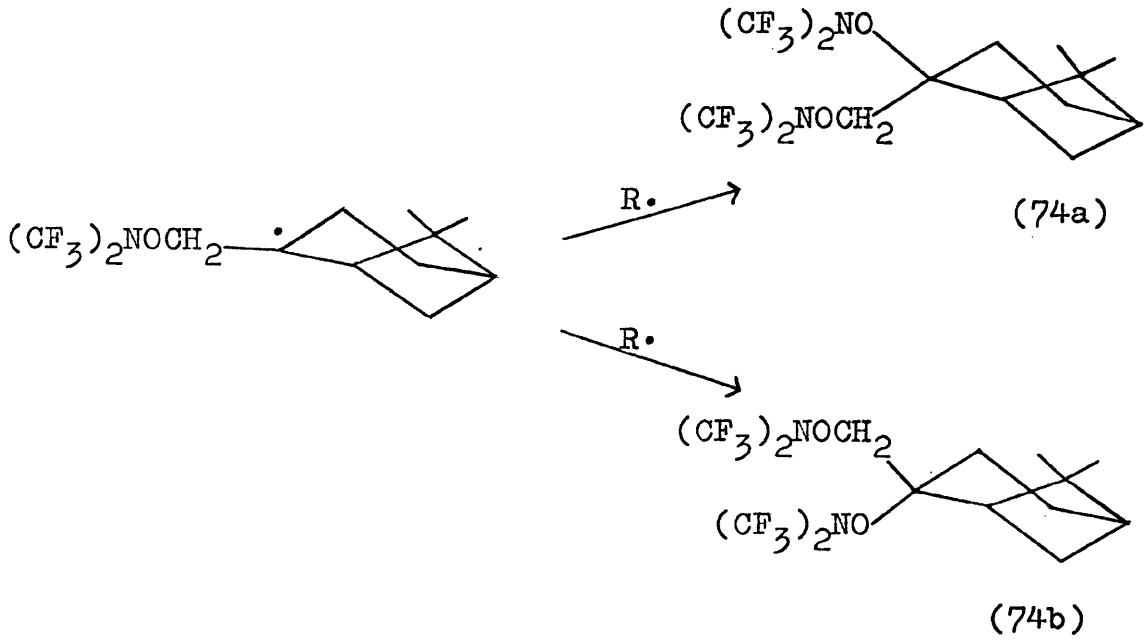
The formation of the products may be explained as outlined in Scheme 12 [where R= $(CF_3)_2NO$].

Addition of the oxyl (6) to the double bond gives intermediate (75) which may be directly scavenged to give the two diastereoisomers (A) and (B) of compound (74), or alternatively, undergo ring opening to give intermediate (76) followed by scavenging by (6) to give the rearranged product (73).

The addition of thiols to 2(10)-pinene has been reported to give only non-rearranged products[69] due to the high concentration of efficient chain-transfer agent. As scavenging of the intermediate radical (75) by the oxyl (6) involves direct coupling of two radicals, the energy of activation of the chain-transfer step is presumably very low,

and the formation of the rearranged product (73), despite the high concentration of oxyl, is probably due to steric interaction which hinders the approach of the relatively bulky $(CF_3)_2NO\cdot$ radical.

Although it was not possible to deduce the stereochemistry of the two disubstituted pinanes (A) and (B) from their n.m.r. spectra, it is considered that the major isomer (B) is the <u>endo</u>-adduct (74b) resulting from chain-transfer with (6) on the side opposite to the $>CMe_2$ bridge. Such attack will involve the least steric hindrance; the minor product (A) is therefore the <u>exo</u>-adduct (74a), <u>i.e</u>.

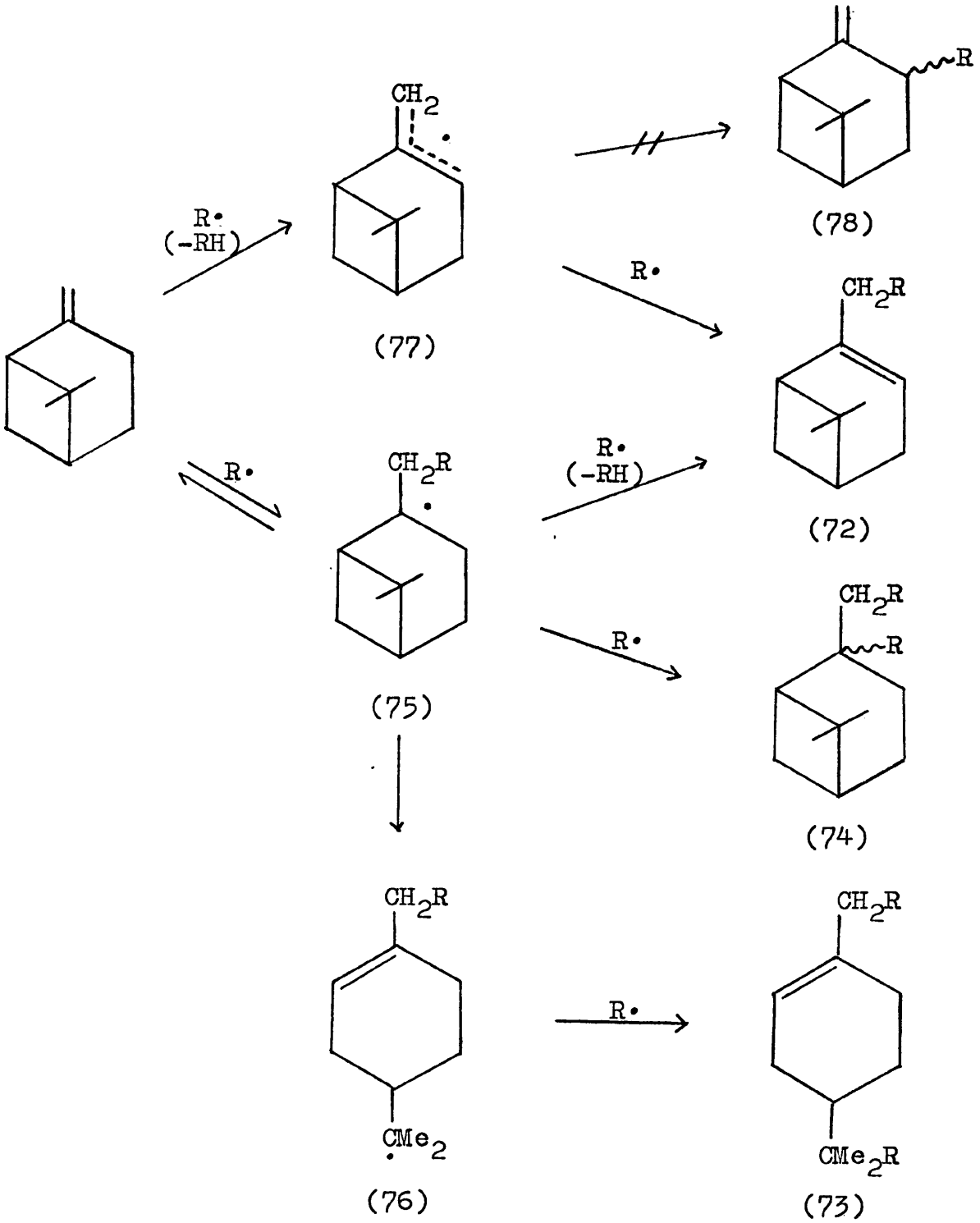


Alternatively, (6) may abstract an allylic hydrogen to give intermediate (77), which then undergoes chain-transfer with (6) at the terminal carbon (<u>i.e</u>. the 10-position) giving the monosubstituted product (72). Surprisingly, none of the

3-substituted isomer (78) was detected amongst the reaction products, and may indicate that an alternative mechanism, involving hydrogen abstraction from intermediate (75) is involved; this is discussed later (p. 119).

On dilution of the reactants the yield of rearranged product (73) did not increase as was expected, but instead the yield of hydrogen abstraction product (72) increased, and this may indicate that the addition of the oxyl (6) is reversible to some extent.

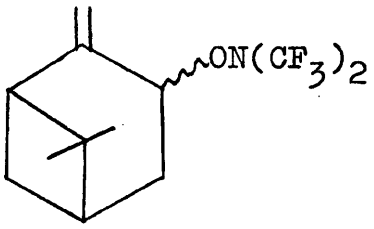
Reaction of the oxyl (6) with 2(10)-pinene



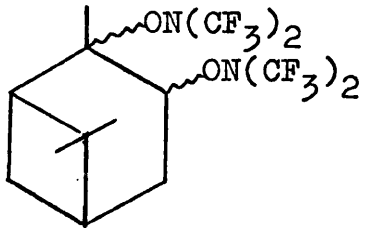
Scheme 12

(ii) With 2-pinene

The reaction of a 2:1 molar mixture of the oxyl (6) and 2-pinene reached completion on warming from -196 °C to room temperature and gave NN-bistrifluoromethylhydroxylamine (37% based on oxyl), unchanged 2-pinene (4.5% recovered), four minor unidentified products, and two amino-oxy-substituted products, which were identified by elemental analysis and the spectroscopic data outlined below as 3-(NN-bistrifluoromethylamino-oxy)-2(10)-pinene (78) (66.5% based on consumed pinene), and 2,3-bis(NN-bistrifluoromethylamino-oxy)pinane (79) (20.5% based on pinene).



(78)



(79)

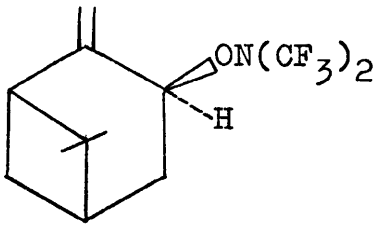
3-(NN-bistrifluoromethylamino-oxy)-2(10)-pinene (78)

The i.r. spectrum showed absorptions at 7.70-8.33 (C-F str.), 9.64 and/or 9.76 (C-O-N str.), 10.36 (C-N str.), and 14.08 (CF_3 def.) μm, characteristic of an amino-oxy group, and other absorptions at 3.25-3.48 (C-H str.), and 6.08 (C:C str.) μm.

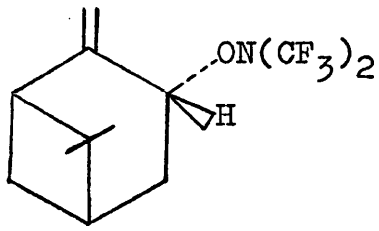
The ^{1}H n.m.r. spectrum showed absorptions at δ 0.44 (s), 1.07 (s), 1.38-2.33 (c), 4.31 (m) and 4.37 (m), and 4.75 (s) and 4.88 (s) p.p.m., integrated intensities 3: 3: 6: 1: 2,

assigned to the two methyl groups, the six ring protons, the methine proton in a $>CHON(CF_3)_2$ group, and the olefinic proton, respectively.

The appearance of two methine signals at δ 4.31 and 4.37 p.p.m. and two olefinic signals at δ 4.75 and 4.88 p.p.m. can be explained by the isolated sample consisting of the two diastereoisomers (78a) and (78b) in the ratio 1:1 (as shown by the integrated intensities). The methine and olefinic protons in each isomer would be expected to have different chemical shifts.



(78a)



(78b)

The ^{19}F n.m.r. spectrum showed two very broad signals at δ 27.8 (-9.5) and 26.6 (-10.7) p.p.m., integrated intensities 1:1, assigned to the fluorines in the sterically hindered amino-oxy group of each diastereoisomer; the lower-field signal is probably due to the more sterically hindered exo-isomer (78a).

The mass spectrum showed peaks at m/e 135 (37%, $C_{10}H_{15}^+$), 107 (33%, $C_8H_{11}^+/C_7H_7O^+$), 93 (92%, $C_7H_9^+/C_6H_5O^+$), 91 (49%, $C_7H_7^+$), and 69 (100%, CF_3^+).

2,3-Bis(NN-bistrifluoromethylamino-oxy)pinane (79)

The i.r. spectrum showed only that it was an amino-oxy-

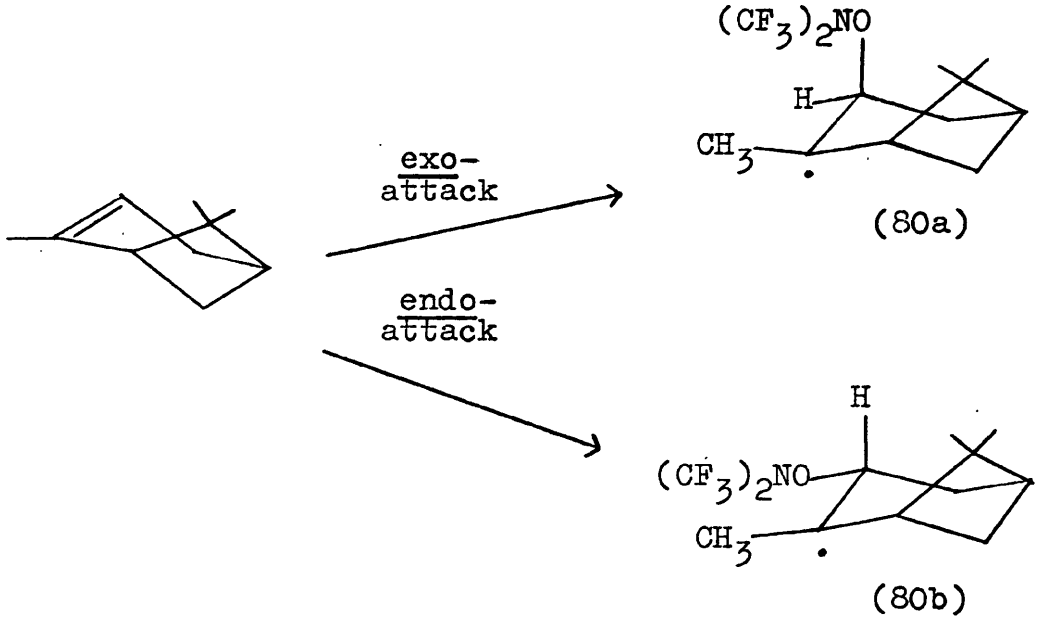
substituted alkane.

The ^{1}H n.m.r. spectrum showed absorptions at δ 0.86 (3H, s), 1.18 (3H, s), 1.38 (3H, s), 1.5-2.5 (6H, c), and ca. 4.6 (1H, m) p.p.m., assigned to the three methyl groups, the seven ring protons, and the methine proton in a $>CHON(CF_3)_2$ group, respectively.

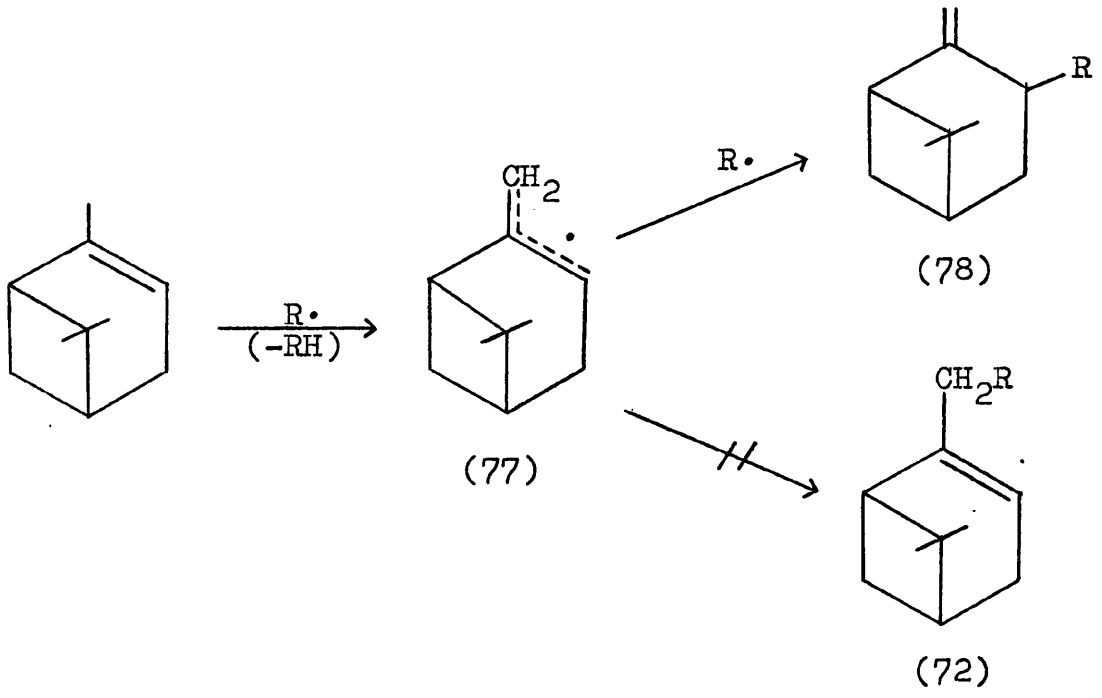
The ^{19}F n.m.r. spectrum showed (i) a broad complex absorption at δ 27.8 (-9.5) p.p.m., and (ii) several overlapping absorptions in the region δ 27.1 (-10.2) to 26.9 (-10.3) p.p.m., integrated intensities 1:1, which can be explained by the isolated sample consisting of several diastereoisomers in which the fluorines in each $>C-ON(CF_3)_2$ group have slightly different chemical shifts.

The mass spectrum showed peaks at m/e 304 {4.5%, $[M-(CF_3)_2NO]^+$}, 152 (5.5%, $C_{10}H_{16}O^+$), 136 (34.5%, $C_{10}H_{16}^+$), and 69 (100%, CF_3^+).

In contrast to the reaction of the oxyl (6) with 2(10)-pinene, the reaction with 2-pinene seemingly did not result in rearrangement, although several minor products were formed which were not identified. The disubstituted pinane (79) which was isolated appeared to be a mixture of several diastereoisomers, indicating that both attack of (6) and chain-transfer occurred from the exo- and endo-sides of the molecule, although it was expected that the approach of (6) would be predominantly on the side opposite to that of the $>CMe_2$ bridge, i.e.

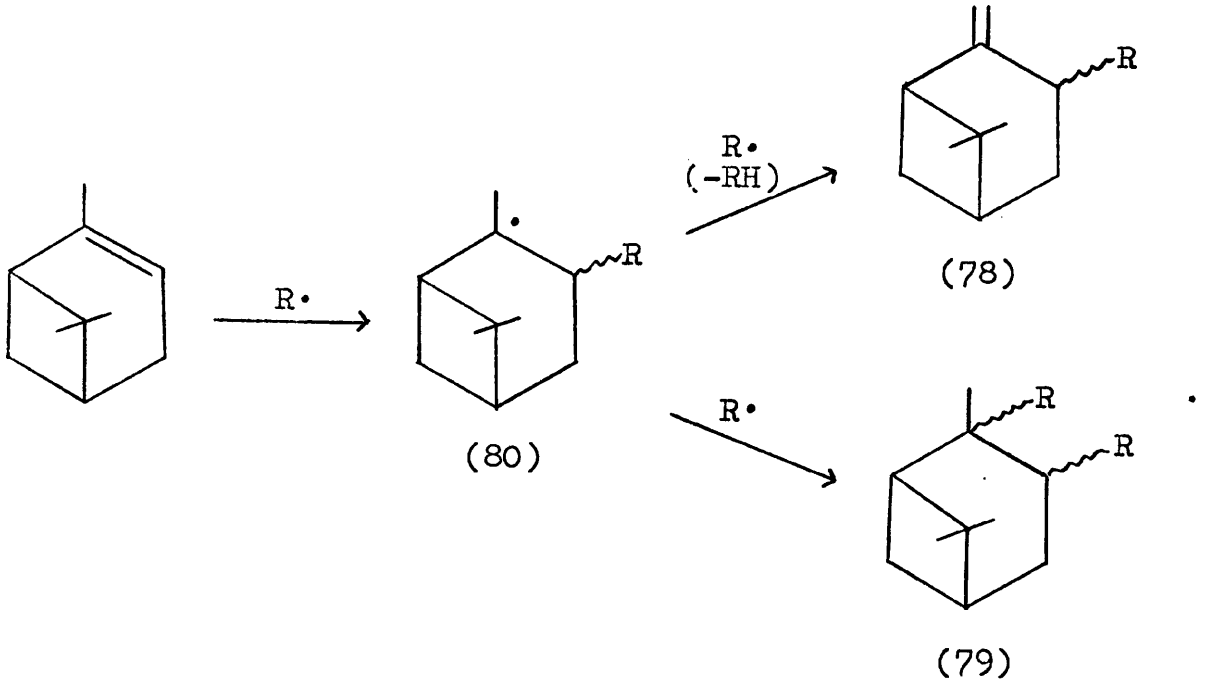


Once again hydrogen abstraction was the major process, but surprisingly only the 3-isomer (78) was obtained, i.e. [where R= $(CF_3)_2NO$]



The 10-isomer (72) was not detected in the reaction products although if a common allylic radical intermediate (77) was involved, as indicated above, it would be expected that chain-transfer with the oxyl (6) would be more favourable at the terminal carbon, as is the case for 2(10)-pinene. Furthermore, recent work has shown that in the reactions of N-bromosuccinimide[69] and t-butyl hypochlorite[109] with 2-pinene, the 10-substituted isomer is obtained as the major product.

An alternative mechanism which may explain the exclusive formation of the monosubstituted isomer (78) is that the oxyl (6) initially adds to the double bond in 2-pinene to give the intermediate radical (80), which may then either couple with (6) to give the disubstituted product (79), or undergo further hydrogen abstraction, i.e. [where R= $(CF_3)_2NO$]



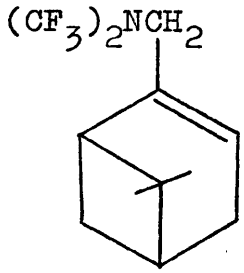
As initial hydrogen abstraction from 2-pinene to give the allylic radical intermediate (77) involves the removal of a primary hydrogen atom, abstraction is not favoured with respect to addition which gives a tertiary radical. However, addition to the intermediate radical (80) is hindered so hydrogen abstraction can now compete with addition to give the monosubstituted product (78).

A similar mechanism may explain the exclusive formation of the 10-substituted isomer (72) in the reaction of the oxyl with 2(10)-pinene. However, as initial hydrogen abstraction from 2(10)-pinene to form the allylic radical intermediate (77) would involve the removal of a secondary hydrogen atom, it may be that initial hydrogen abstraction is more favourable in this case, and that abstraction may successfully compete with addition.

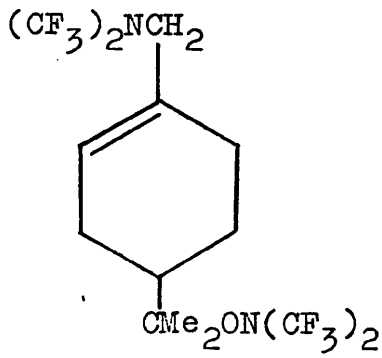
(b) The reactions of the oxadiazapentane (7) with pinenes

(i) With 2(10)-pinene

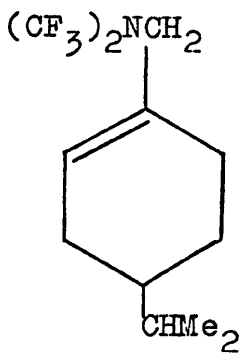
The reaction between an equimolar mixture of (7) and 2(10)-pinene at room temperature (6d) gave a complex mixture of products which included NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, and four products tentatively identified as 10-NN-bistrifluoromethylamino-2-pinene (81) (ca. 15% based on pinene), 10-(NN-bistrifluoromethylamino-oxy)-2-pinene (72) (ca. 7% based on pinene), 1-NN-bistrifluoromethylaminomethyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene (82) (ca. 10% based on pinene), and 1-NN-bistrifluoromethylaminomethyl-4-isopropylcyclohex-1-ene (83) (ca. 20% based on pinene).



(81)



(82)



(83)

Products (81) and (72) were isolated together and identified from the spectral data of the two-component mixture [product (72) having been obtained previously in the reaction of the oxyl (6) with 2(10)-pinene (p. 108)]. The rearranged products (82) and (83) could not be isolated pure and as a result the microanalysis results for the two compounds were slightly different to the figures required.

10-NN-bistrifluoromethylamino-2-pinene (81) and 10-(NN-bistrifluoromethylamino-oxy)-2-pinene (72)

The i.r. spectrum of the mixture showed absorptions in the regions 3.29-3.52 (C-H str.), 6.05 (C:C str.), 7.27-8.62 (C-F str.), 9.62 (C-O-N str.), 10.34 (C-N str.), and 14.08 and 14.39 (CF_3 def.)μm, which were expected for an alkene containing both $(CF_3)_2N$ and $(CF_3)_2NO$ groups.

The ^1H n.m.r. spectrum showed absorptions at δ 0.61 (3H, s), 1.06 (3H, s), and 1.4-2.35 (6H, c) p.p.m., assigned to the two methyl groups and the ring protons in both products, and at δ 3.37 (2H, bs) and 5.23 (1H, m) p.p.m., assigned to the $-CH_2N(CF_3)_2$ group and the olefinic proton, respectively, in product (81), and at δ 4.1 (2H, bs) and 5.35 (1H, m) p.p.m.

assigned to the $-CH_2ON(CF_3)_2$ group and the olefinic proton, respectively, in the amino-oxy-substituted product (72)

The ^{19}F n.m.r. spectrum showed singlet absorptions at δ 18.14 (-19.1) p.p.m., assigned to the fluorines in the $(CF_3)_2NCH_2$ group of product (81), and at δ 28.92 (-8.4) p.p.m. assigned to the $(CF_3)_2NOCH_2$ group of product (72).

The mass spectrum showed peaks at m/e 135 (10%, $C_{10}H_{15}^+$), 91 (90%, $C_7H_7^+$), and 69 (49%, CF_3^+), assigned to both products, at m/e 303 (1%, $C_{12}H_{15}F_6NO^+$) and 288 (1%, $C_{11}H_{12}F_6NO^+$), assigned to the amino-oxy-substituted product (72), and at m/e 287 (3%, $C_{12}H_{15}F_6N^+$) and 272 (3%, $C_{11}H_{12}F_6N^+$), assigned to product (81).

1-NN-bistrifluoromethylaminomethyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl] cyclohex-1-ene (82)

The i.r. spectrum of the compound was not recorded, since it could not be obtained pure.

The ^1H n.m.r. spectrum showed absorptions at δ 1.04 (6H, s), ca. 1.3-2.1 (7H, c), 3.44 (2H, bs), and 5.43 (1H, m) p.p.m., assigned to two equivalent methyl groups, seven ring protons, a $-CH_2N(CF_3)_2$ group and an olefinic proton, respectively.

The ^{19}F n.m.r. spectrum showed singlet absorptions at δ 26.6 (-10.7) and 18.4 (-18.9) p.p.m., integrated intensities 1:1, assigned to the fluorines in the $(CF_3)_2NOCMe_2$ group, and $(CF_3)_2NCH_2$ group, respectively.

The mass spectrum showed peaks at m/e 288 {19%, $[M-(CF_3)_2NO]^+$}, 246 {4%, $[M-(CF_3)_2NOCMe_2]^+$}, 210 [22%, $(CF_3)_2NOCMe_2^+$], 166 [100%, $(CF_3)_2NCH_2^+$], 136 (5%, $C_{10}H_{16}^+$),

and 121 (36%, $C_9H_{13}^+$)

1-NN-bistrifluoromethylaminomethyl-4-isopropylcyclohex-1-ene (83)

The i.r. spectrum was not recorded since the compound could not be obtained pure.

The ^1H n.m.r. spectrum showed absorptions at δ 0.64 (3H, s), 0.70 (3H, s), ca. 0.9-2.0 (8H, c), 3.40 (2H, bs), and ca. 5.4 (1H, m) p.p.m., assigned to the methyl groups, eight methylene and methine protons, the protons in a $-CH_2N(CF_3)_2$ group, and an olefinic proton, respectively.

The ^{19}F n.m.r. spectrum showed a singlet absorption at δ 18.4 (-18.9) p.p.m., in the region expected for fluorines in a $(CF_3)_2N$ group.

The mass spectrum showed peaks at m/e 289 (14%, M^+), 274 [2.5%, $(M-CH_3)^+$], 246 [5.5%, $(M-CHMe_2)^+$], 166 [91%, $(CF_3)_2NCH_2^+$], 137 (12.5%, $C_{10}H_{17}^+$), and 67 (100%, $C_5H_7^+$).

The formation of the isolated products may be explained by the mechanism outlined in Scheme 13.

As expected, the yield of rearranged products was higher than that for the corresponding oxyl reaction, due to the slower rate of chain-transfer because of the relatively more hindered approach of the bulky $(CF_3)_2NON(CF_3)_2$ molecule towards intermediate (84).

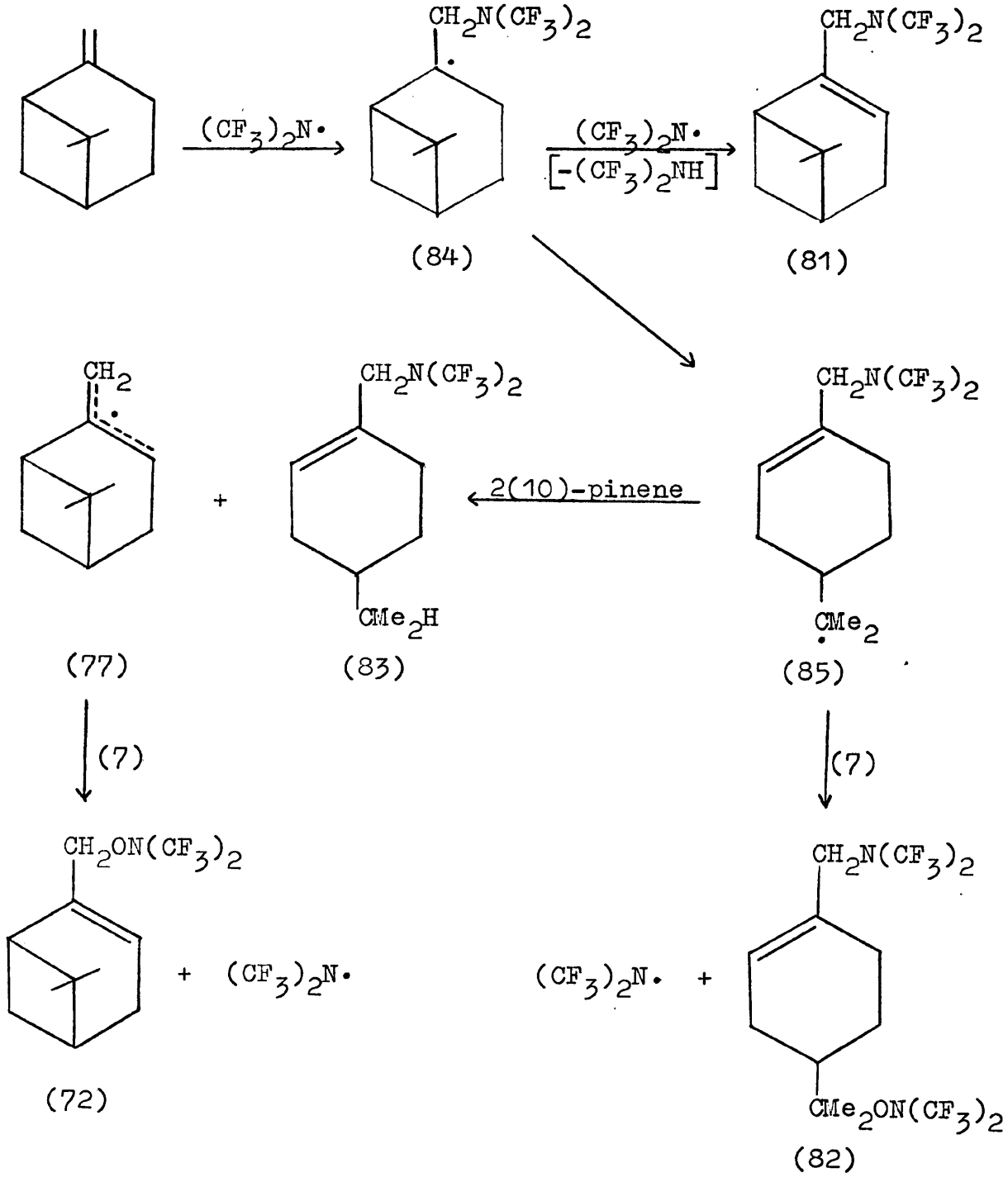
On ring opening, the rearranged radical (85) may undergo chain-transfer with the oxadiazapentane (7) to give product (82), or abstract a hydrogen atom from the starting olefin to give an allylic radical (77) and the monosubstituted

product (83). This competition between the intermediate radical undergoing chain-transfer with (7) and abstracting an allylic hydrogen atom from the starting olefin has recently been observed in the reaction of the oxadiazapentane (7) with cyclohexene[93] and is probably a consequence of steric effects in the approach of the bulky oxadiazapentane molecule. Reaction of the allylic radical (77) with (7) then gives the monosubstituted amino-oxy product (72).

The intermediate allylic radical (77) may also arise *via* hydrogen abstraction by the $(CF_3)_2N\cdot$ radical, although this is less probable as the $(CF_3)_2N\cdot$ radical is known to preferentially undergo addition, at least with acyclic alkenes (*e.g.* penta-1,4-diene and allylbenzene). However, the complexity of the products may be due in part to non-allylic hydrogen abstraction by the intermediate (85) and also to some extent by the non-rearranged intermediate (84).

The formation of the bistrifluoromethylamino-substituted pinene (81) in reasonable yield is rather more difficult to explain, although it is possible that it arises *via* disproportionation of the intermediate radical (84), as suggested may occur in the corresponding oxyl reaction.

Reaction of the oxadiazapentane (7) with 2(10)-pinene



Scheme 13

(ii) With 2-pinene

The reaction between an equimolar mixture of the oxadiazapentane (7) and 2-pinene at room temperature gave NN-bistrifluoromethylamine (ca. 23% based on oxadiazapentane), NN-bistrifluoromethylhydroxylamine [ca. 22% based on (7)], and a complex mixture of ca. thirteen unidentified products which could not be separated or identified.

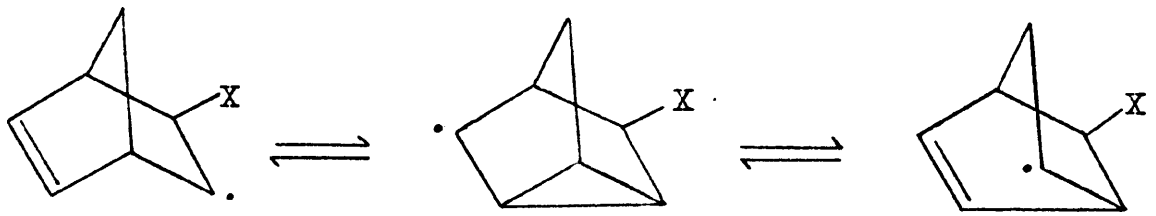
It was rather difficult to determine when the reaction had reached completion and it was worked up after fifteen days.

C. Cyclisation

1. Norbornadiene

The well-documented rearrangement of homoallylic norbornyl radicals (86) to nortricycyl radicals (87) via ring closure is intimately bound with the ring opening of cyclopropylcarbinyl radicals (p. 97) and the migration of vinyl groups.

Experimental data supports the existence of discrete radicals in equilibrium (in which the nortricycyl radical is generally favoured), and that, at least with norbornyl derivatives having bulky C_5 or C_7 substituents, a third radical (88) may be involved, i.e.



(86) (87) (88)

The ratio of products obtained in radical additions depends on whether this equilibrium can be established, and on the environment at the radical site. Hence, the reactions of the oxyl (6) and oxadiazapentane (7) with norbornadiene were studied under various conditions to investigate the extent of rearrangement.

(a) The reaction of the oxyl (6) with norbornadiene

The results of the reactions of the oxyl (6) with norbornadiene under various conditions are summarised in Table 8. The liquid-phase reactions were carried out in low-temperature slush baths as it was found that the reaction of a neat mixture of (6) and norbornadiene reached completion on warming from -196 °C to room temperature and gave a black, charred mixture of products.

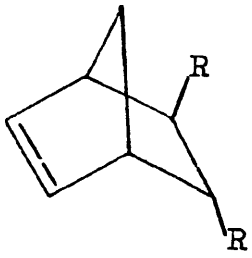
Products (B) and (C) were identified as 2-exo-3-endo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene (89) and 2,3-exo-exo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene (90), respectively, on the basis of elemental analysis and the spectroscopic data outlined below. Products (D) and (E) were not isolated but were tentatively identified as 2-exo-6-endo- (91) and 2-exo-6-exo-bis(NN-bistrifluoromethylamino-oxy)nortricyclane (92) on the basis of their coupled g.l.c./mass spectra. The higher-boiling products (F-I) were similarly tentatively identified as four of the eight possible diastereoisomers of 2-exo-3,5,6-tetrakis(NN-bistrifluoromethylamino-oxy)norbornane (93).

TABLE 8

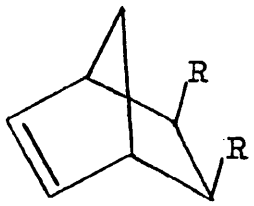
Reaction of the oxyl (6) with norbornadiene

	1	2	3	4
Conditions	neat liquid	solution[a]	solution[a]	gas phase
Temperature (°C)	-64	-78	-64	(b)
Ratio of oxyl:diene	1.6:1	2:1	1:19	2:1
Reaction time	2h	40min	1.5h	(b)
Recovered diene (%)	ca.32	(c)	(c)	(c)
Involatile products	(d)	(d)	(d)	(d)
B (89)	32	27	41	20
C (90)	28	34	39	15.5
D (91)	14	8.5	9	30.5
E (92)	10	7.5	8	22
F	5	13	-	-
G	2	4	-	-
(93)				
H	1.5	3	-	-
I	1.5	3	-	-

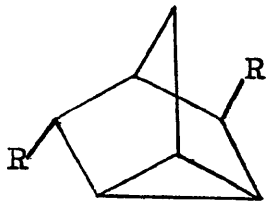
(a) Reaction carried out in solution of 1,1,2-trichloro-1,2,2-trifluoroethane.
(b) Reaction complete on warming from -196 °C to room temperature.
(c) Not determined.
(d) Ratio of products.



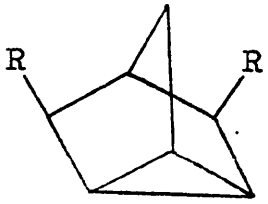
(89)



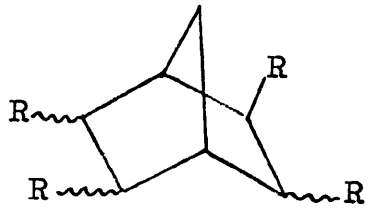
(90)



(91)



(92)



(93)

$[R = (CF_3)_2NO]$

Product (B): 2-exo-3-endo-bis(NN-bistrifluoromethylamino-oxy)-norborn-5-ene (89)

The i.r. spectrum showed absorptions at 3.25-3.47 (C-H str.), 6.10-6.33 (C:C str.), 7.70-8.31 (C-F str.), 9.51 and 9.61 (C-O-N str.), 10.35 (C-N str.), 10.88-12.90 (C-H def.), and 13.77 and 14.08 (CF_3 def. and/or C-H def.)μm, typical of an amino-oxy-substituted alkene.

The ^1H n.m.r. spectrum showed absorptions at δ 1.54 (2H, s), 2.79 (2H, c), 3.85 (1H, s), 4.37 (1H, bs), and 5.91 (2H, m) p.p.m., assigned to methylene, methine, two non-equivalent protons in two $>CHON(CF_3)_2$ groups, and two olefinic protons, respectively.

The ^{19}F n.m.r. spectrum showed absorptions at δ 29.2 (-8.1) (s), and 29.0 (-8.3) (bs) p.p.m., integrated intensities 1:1, assigned to the fluorines of the two non-equivalent endo- and exo- $(CF_3)_2NOCH$ groups, respectively.

The mass spectrum showed peaks at m/e 260 {1%, $[M-(CF_3)_2NO]^+$}, 108 (12%, $C_7H_8O^+$), 92 (3%, $C_7H_8^+$), 79 (14%, $C_6H_7^+$), 66 (100%, $C_5H_6^+$), and 28 (5%, $C_2H_4^+$).

Product (C): 2,3-exo-exo-bis(NN-bistrifluoromethylamino-oxy)-norborn-5-ene (90)

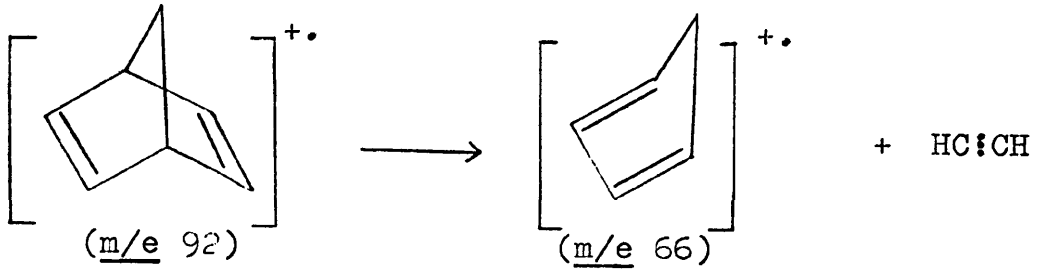
The i.r. spectrum showed absorptions typical of an amino-oxy group together with bands at 3.25-3.47 (C-H str.), 6.12-6.33 (C:C str.), 10.64-12.90 (C-H def.), and 13.77 and 14.08 (CF_3 def. and/or C-H def.)μm.

The ^1H n.m.r. spectrum showed absorptions at δ ca. 1.7 (2H, c), 2.90 (2H, bs), 4.02 (2H, s), and 5.86 (2H, m) p.p.m., assigned to methylene protons, methine protons, two $>CHON(CF_3)_2$ groups, and two olefinic protons, respectively.

The ^{19}F n.m.r. spectrum showed a broad absorption at δ 28.85 (-8.4) p.p.m., assigned to the fluorines in two relatively hindered equivalent amino-oxy groups.

The fragmentation pattern in the mass spectrum was virtually identical to that of the exo-endo-isomer (89), with additional peaks at m/e 427 [1%, $(M-H)^+$], and 402 [1%, $(M-C_2H_2)^+$].

The base peak at m/e 66 observed in the mass spectra of the two norbornene derivatives (89) and (90) is probably due to fragmentation via a retro-Diels-Alder mechanism, i.e.



(m/e 92) (m/e 66)

Products (D) and (E): 2-exo-6-endo- (91) and 2-exo-6-exo-bis(NN-bistrifluoromethylamino-oxy)nortricyclane (92)

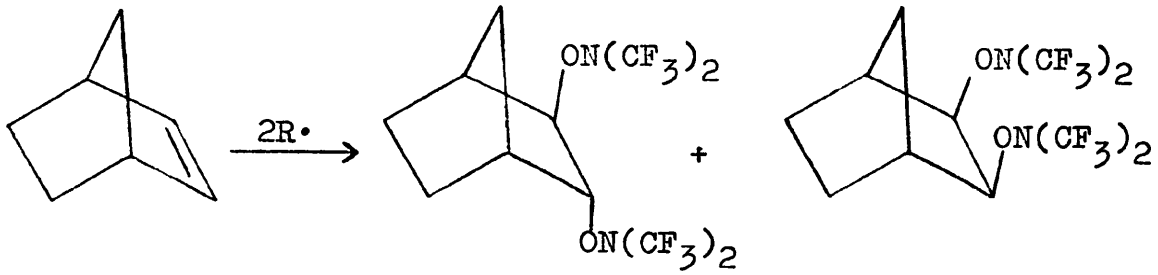
In contrast to the norbornene derivatives (89) and (90), products (D) and (E) both showed base peaks at m/e 79 (100%, $C_6H_7^+$), together with peaks at m/e 260 {35%, $[M-(CF_3)_2NO]^+$}, 108 (50%, $C_7H_8O^+$), 92 (16%, $C_7H_8^+$), and 66 (92%, $C_5H_6^+$). The intensities given are for product (D) although the values for product (E) were very similar.

Products (F-I): 2-exo-3,5,6-tetrakis(NN-bistrifluoromethylamino-oxy)norbornane (93)

The mass spectra of the four products were very similar and showed peaks (e.g. for product F) at m/e 596 {6%, $[M-(CF_3)_2NO]^+$}, 428 (12%, $C_{11}H_8F_{12}N_2O_2^+$), 276 (19%, $C_9H_8F_6NO_2^+$), 260 (33%, $C_9H_8F_6NO^+$), 124 (43%, $C_7H_8O_2^+$), 108 (46%, $C_7H_8O^+$), 79 (83%, $C_6H_7^+$), 69 (100%, CF_3^+), and 66 (52%, $C_5H_6^+$).

The formation of the products may be explained by the mechanism outlined in Scheme 14 [where R= $(CF_3)_2NO$].

Although radical attack on norbornadiene (and norbornene) is believed to be predominantly from the exo- direction, due to steric interference between the endo-5-hydrogens and the attacking radical, chain-transfer may occur from both the exo- and endo- directions.[111] Brown has reported[83] that the reaction of the oxyl (6) with norbornene gave the trans- and cis-adducts (94) and (95) in the ratio 1.3: 1, i.e.



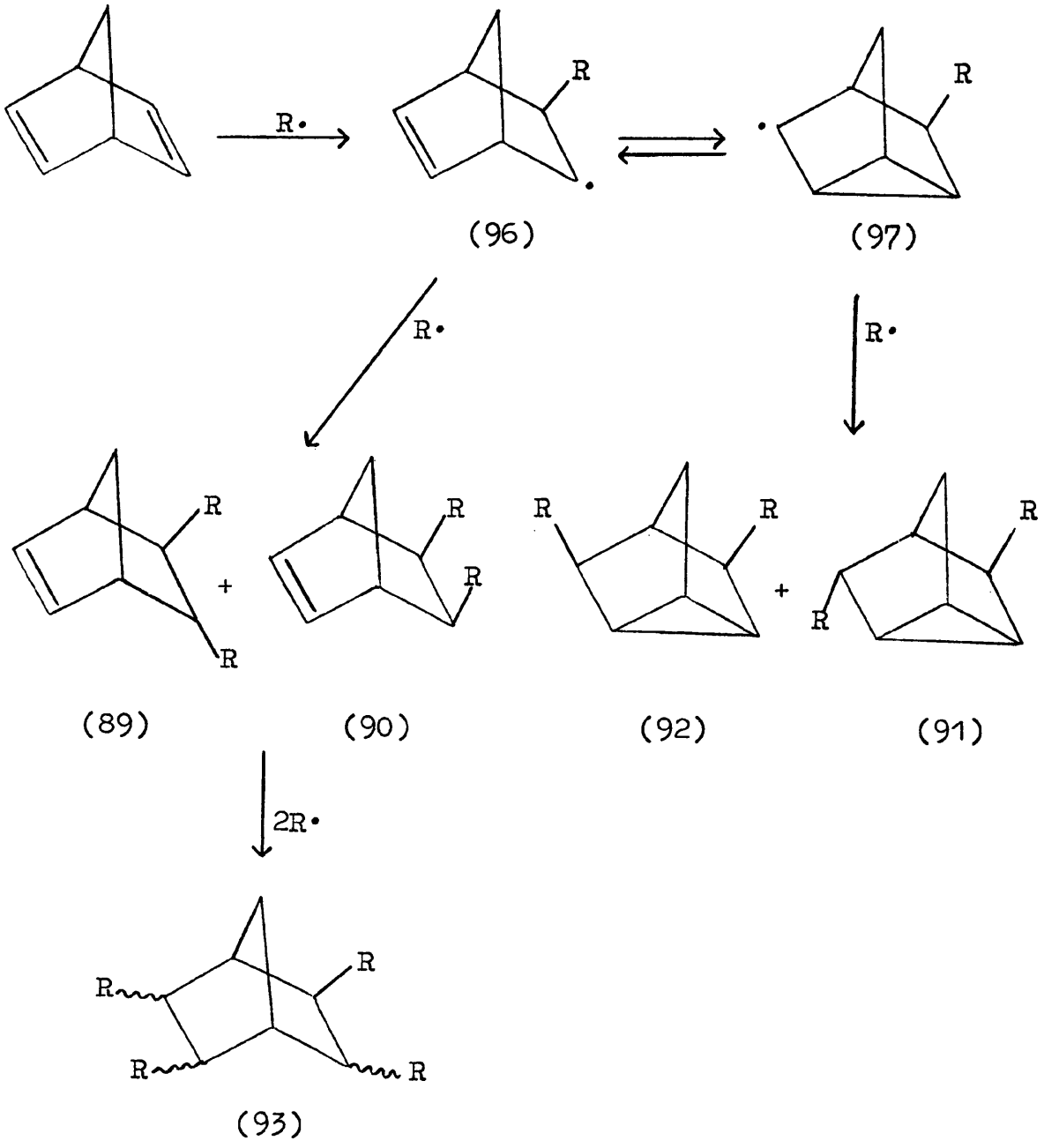
(94) (95)

The ratio of norbornene derivatives (89) and (90) obtained in the reactions of the oxyl (6) with norbornadiene under various conditions did not vary considerably from ca. 1:1, and indicates that chain-transfer by the oxyl with intermediate (96) is equally favourable from both the exo- and endo- directions.

Alternatively, the intermediate radical (96) may rearrange to the nortricycyl radical (97), and in the gas-phase, where the relatively low concentration of (6) allows the equilibrium to be established, it was found that the relative yields of nortricyclane derivatives (91) and (92) were increased at the expense of the norbornene derivatives (89) and (90).

The reactivity of each double bond in norbornadiene is believed to be only about equal to that of the double bond in norbornene[111] and consequently it is suggested that the higher-boiling products (F-I) are formed via further attack of (6) on the norbornene derivatives (89) and (90). In support of this, when an excess of diene was used, or when the reaction was carried out in the gas phase, the higher-boiling products were not detected.

Reaction of the oxyl (6) with norbornadiene



Scheme 14

(b) The reaction of the oxadiazapentane (7) with norbornadiene

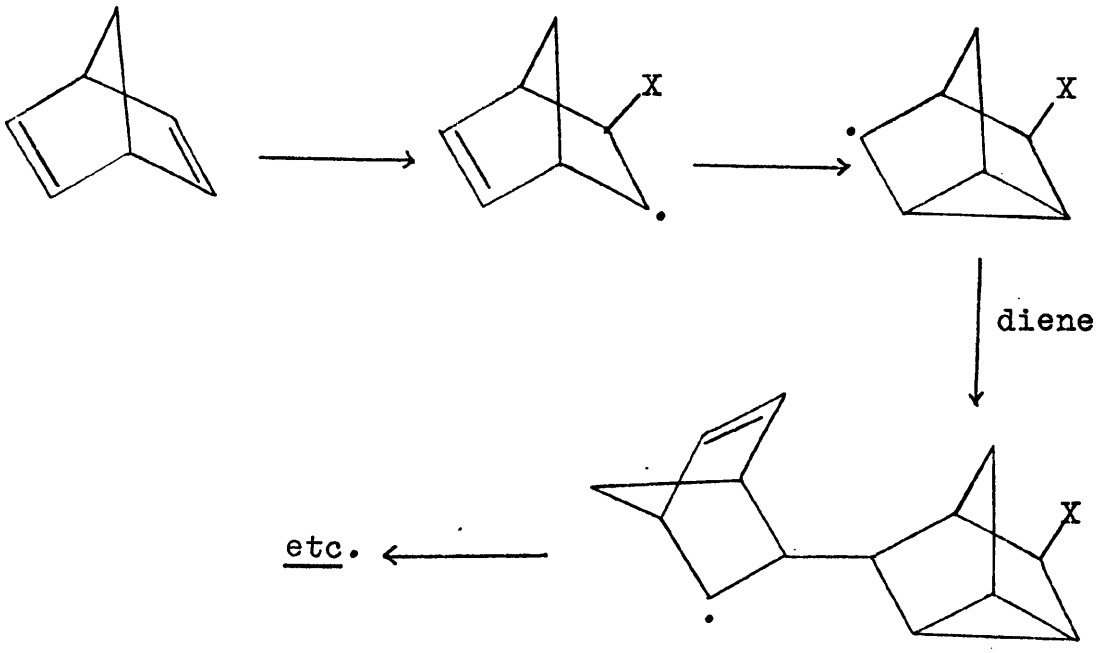
The reaction of an equimolar mixture of the oxadiazapentane (7) and norbornadiene in 1,1,2-trichloro-1,2,2-trifluoroethane at room temperature (ca. 8d) gave, on removal of the lower-boiling material, a yellow gelatinous solid which could not be separated by column chromatography or by t.l.c. (using acetone, chloroform or 1,1,2-trichloro-1,2,2-trifluoroethane as eluants).

The i.r. and n.m.r. spectra of the material were very complex and poorly resolved and showed only that it was an amino- and amino-oxy-substituted alkane. The mass spectrum of the mixture showed peaks at m/e 580 (1%, $C_{13}H_8F_{18}N_3O_2^+$), 503 (1%, $C_{18}H_{15}F_{12}N_2O^+$), 427 (1%, $C_{23}H_{23}F_6N^+/C_{11}H_8F_{12}N_2O_2^+$), 412 (1%, $C_{11}H_8F_{12}N_2O^+$), 336 (1%, $C_{16}H_{16}F_6N^+$), 275 (1%, $C_{21}H_{23}^+$), 260 (2.5%, $C_9H_8F_6NC^+/C_{20}H_{20}^+$), 244 (22%, $C_9H_8F_6N^+$), 184 (1.5%, $C_{14}H_{16}^+$), and 69 (100%, CF_3^+). It is considered that the material contained telomers of the general formulae $(CF_3)_2N(C_7H_8)_nON(CF_3)_2$ (where n=1,2,...), together with bis(NN-bistrifluoromethylamino-oxy)-NN-bistrifluoromethylamino-substituted norbornene units.

The material was dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane and on removal of the solvent by condensation in vacuo the residual lower-boiling material 'trapped' in the gelatinous material was removed, and gave a white solid; the i.r. and n.m.r. of which were very complex and therefore the material was not investigated further.

Norbornadiene may undergo polymerisation under suitable

free-radical conditions to form soluble low molecular weight polymers.[112] In contrast, norbornene does not polymerise readily and thus it is believed that the nortricycyl radical is involved in the prop gation step in the polymerisation reaction, although the resultant polymer may be composed mainly of 5,6-disubstituted norbornene units,[113] or alternating 5,6-disubstituted norbornene and 3,5-disubstituted nortricyclane units,[112] i.e.



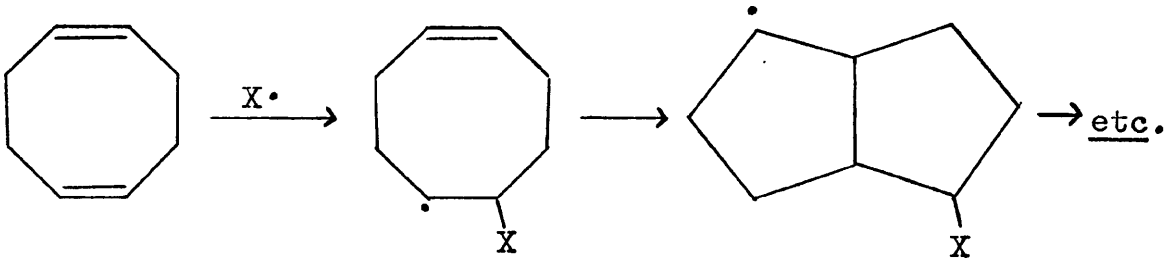
Although the nortricyclane structure is favoured energetically, it is believed that a polymer composed entirely of nortricyclane units would be subject to considerable strain.

It is considered that polymerisation occurs in the reaction of the oxadiazapentane (7) with norbornadiene as a result of the slow rate of chain-transfer; the unreacted (7) may then undergo 1,2-addition to the unsaturated norbornene

units in the polymer chains which explains the peaks in the mass spectrum at m/e 580, 503 and 427.

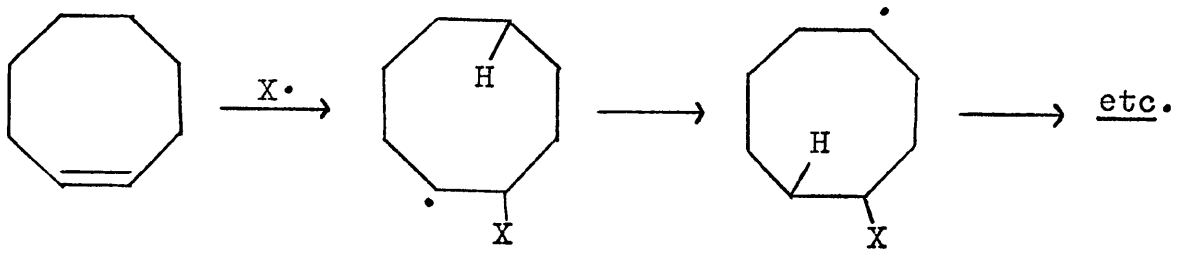
2. Octenes.

Under suitable free-radical conditions, cyclo-octa-1,5-diene undergoes ring closure to give bicyclo-[3.3.0]-octanes, i.e.



As expected, the extent of ring closure is dependent both on the temperature and on the concentration and efficiency of the chain-transfer agent.

In the present work, the reaction of cis-cis-cyclo-octa-1,5-diene with the oxyl (6) and with the oxadiazapentane (7) were studied. The reaction of the oxyl (6) with cyclo-octene was also investigated to determine whether products arising from a 1,5-shift of hydrogen were formed, i.e.



Although not strictly a ring-closure reaction (as

cyclisation does not occur), the six-membered transition state involved in the rearrangement step is believed to allow an approach to colinearity for the transfer of hydrogen, which favours the transannular rearrangement.

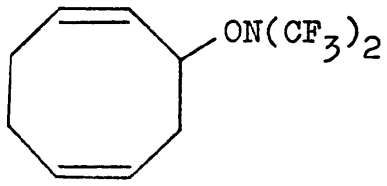
(a) (i) Reaction of the oxyl (6) with cis-cis-cyclo-octa-1,5-diene

The reaction of a 2:1 molar mixture of the oxyl (6) and the diene reached completion on warming from -196 °C to room temperature and gave NN-bistrifluoromethylhydroxylamine (43.5 % based on oxyl), unchanged diene (35% recovered), and a complex mixture of higher-boiling products from which were separated (i) an unidentified monosubstituted NN-bistrifluoromethylamino-oxy)cyclo-octene derivative (A) (30% based on consumed diene), (ii) a mixture of two products (B) and (C) (ca. 1:1 ratio), tentatively identified as a bis(amino-oxy)cyclo-octadiene (ca. 13%) and a bis(amino-oxy)cyclo-octene (ca. 16% based on consumed diene), and (iii) a mixture of two products (D) and (E) tentatively identified as a bis(amino-oxy)cyclo-octadiene (ca. 13%) and a bis(amino-oxy)-cyclo-octene (ca. 16% based on consumed diene)(ca. 1:1 ratio).

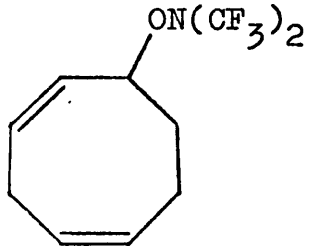
A coupled g.l.c./mass spectrum of the mixture was recorded, but adequate separation of the products could not be achieved.

The monosubstituted product (A) was identified by elemental analysis and the spectroscopic data outlined below. Although the ^{1}H n.m.r. spectrum was not sufficiently clear to allow the determination of the position of substitution, it is considered that of the two isomers that may be formed as a

result of scavenging of the allylic intermediate (98) by the oxyl (Scheme 15), 3-(NN-bistrifluoromethylamino-oxy)cyclo-octa-1,5-diene (99) is the more probable, as molecular models show that the other possible isomer, the cyclo-octa-1,4-diene derivative (100), is subject to considerable ring strain.



(99)



(100)

The i.r. spectrum showed the characteristic absorptions of an amino-oxy group together with bands at 3.33-3.53 (C-H str.), and 6.02 (C:C str.)μm.

The ^{1}H n.m.r. spectrum showed absorptions at δ ca. 1.7-2.6 (6H, c), ca. 4.8 (1H, m) and ca. 5.3 (4H, c) p.p.m., assigned to the methylene protons, the $>CHON(CF_3)_2$ group, and the olefinic protons, respectively, while the ^{19}F n.m.r. spectrum showed a singlet absorption at δ 28.5 (-8.8) p.p.m., characteristic of the fluorines in an amino-oxy group.

The mass spectrum showed peaks at m/e 275 (2%, M^+), 123 (2.5%, $C_8H_{11}O^+$), 107 (100%, $C_8H_{11}^+$), 79 (94%, $C_6H_7^+$), and 69 (67%, CF_3^+).

Products (B) and (C) were isolated together and identified from the spectral data of the two-component mixture. The elemental analysis figures obtained for the mixture showed it to contain compounds of formulae

$C_{12}H_{12}F_{12}N_2O_2$ and/or $C_{12}H_{10}F_{12}N_2O_2$.

The i.r. spectrum of the two-component mixture showed absorptions typical of an amino-oxy group, together with bands at 3.30-3.48 (C-H str.) and 6.08 (C:C str.)μm.

The ^1H n.m.r. spectrum was poorly resolved and showed broad complex absorptions at δ ca. 1.0-2.6 (12H, c), ca. 4.2 (2H, c), ca. 4.6-5.0 (2H, c), and ca. 5.2-5.8 (6H, c) p.p.m., assigned to twelve methylene protons, four $>CHON(CF_3)_2$ groups, and six olefinic protons, respectively, in the two compounds.

The ^{19}F n.m.r. spectrum showed several overlapping absorptions at δ ca. 28.8 (-8.5) p.p.m., in the region expected for fluorines in amino-oxy groups.

The mass spectrum showed peaks (i) at m/e 79 (100%, $C_6H_7^+$) and 69 (70%, CF_3^+) which were assigned to both compounds, (ii) at m/e 290 (1%, $C_{10}H_{10}F_6NO_2^+$), 274 (4%, $C_{10}H_{10}F_6NO^+$), 260 (1%, $C_9H_8F_6NO^+$), 122 (13%, $C_8H_{10}O^+$), and 106 (51%, $C_8H_{10}^+$), assigned to the cyclo-octadiene derivative (B), and (iii) at m/e 276 (1.5%, $C_{10}H_{12}F_6NO^+$), 262 (1%, $C_9H_{12}F_6NO^+$), 124 (20%, $C_8H_{12}O^+$), and 108 (11%, $C_8H_{12}^+$), which were assigned to the cyclo-octene derivative (C).

Products (D) and (E) were isolated together and identified by spectroscopic data obtained for the two-component mixture. The elemental analysis figures of the mixture indicated that it was a mixture of compounds of formulae $C_{12}H_{12}F_{12}N_2O_2$ and/or $C_{12}H_{10}F_{12}N_2O_2$.

The i.r. spectrum of the two-component mixture showed the characteristic absorptions of an amino-oxy group,

together with bands at 3.29-3.51 (C-H str.) and 6.04 (C:C str.)μm.

The ^{1}H n.m.r. spectrum showed broad complex absorptions at δ ca. 1.2-2.4 (12H), 4.12 (2H), ca. 4.8 (2H), and ca. 5.2-5.8 (6H) p.p.m., assigned to twelve methylene protons, four $CHON(CF_3)_2$ groups, and six olefinic protons, respectively, in the two compounds.

The ^{19}F n.m.r. spectrum showed (i) a broad complex absorption at δ 28.5 (-8.9) p.p.m., and (ii) several overlapping absorptions at δ ca. 28.8 (-8.5) p.p.m., integrated intensities ca. 1:1, in the region expected for fluorines in amino-oxy groups.

The mass spectrum showed peaks at (i) m/e 425 (1%, $C_{12}H_{12}F_{11}N_2O_2^+$), 292 (1%, $C_{10}H_{12}F_6NO_2^+$), 276 (1%, $C_{10}H_{12}F_6NO^+$), assigned to the cyclo-octene derivative (E), (ii) at m/e 290 (1%, $C_{10}H_{10}F_6NO_2^+$), and 274 (1%, $C_{10}H_{10}F_6NO^+$), assigned to the cyclo-octadiene derivative (D), and (iii) at m/e 69 (100%, CF_3^+), assigned to both compounds.

The formation of the products may be explained by the mechanism outlined in Scheme 15 [where R= $(CF_3)_2NO$].

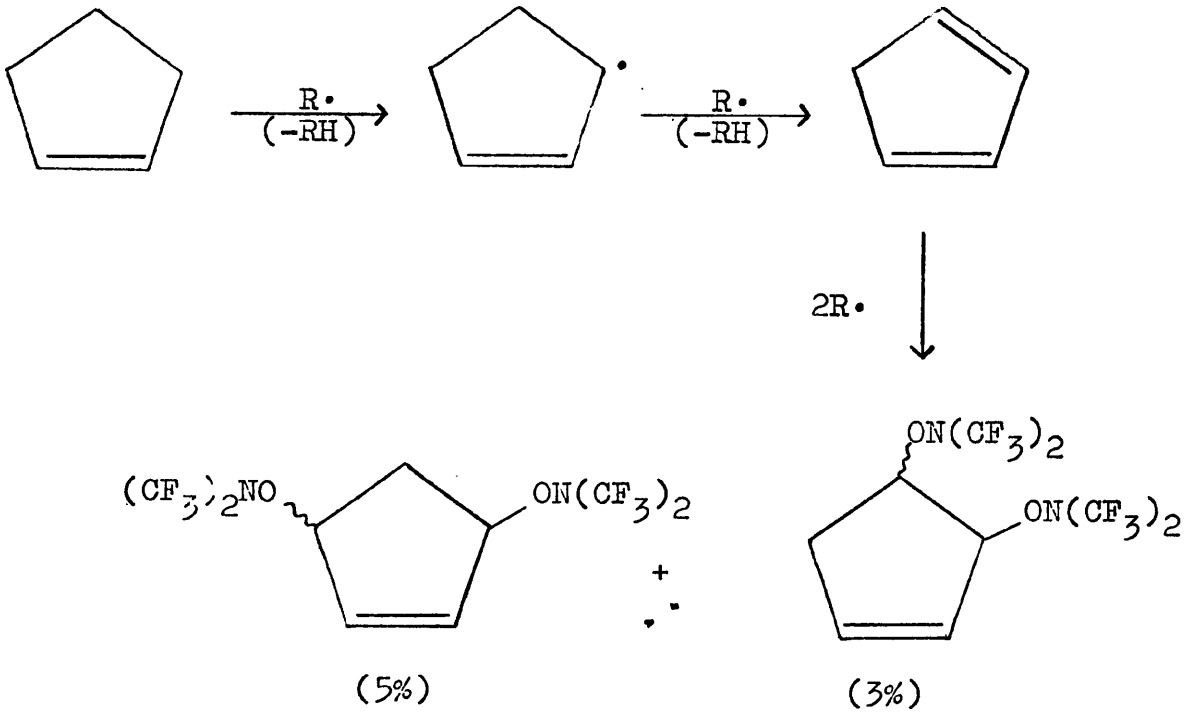
The isolated products represent a reasonable yield (ca. 86%) and although products (B-E) could not be isolated pure, the ^{1}H n.m.r. spectra of the two mixtures showed strong absorptions in the region expected for olefinic protons, indicating that cyclisation had not occurred.

Unlike the reaction of the oxyl (6) with cyclo-octene (p. 149) where only one disubstituted product (probably the trans-adduct) was obtained in reasonable yield, evidence was

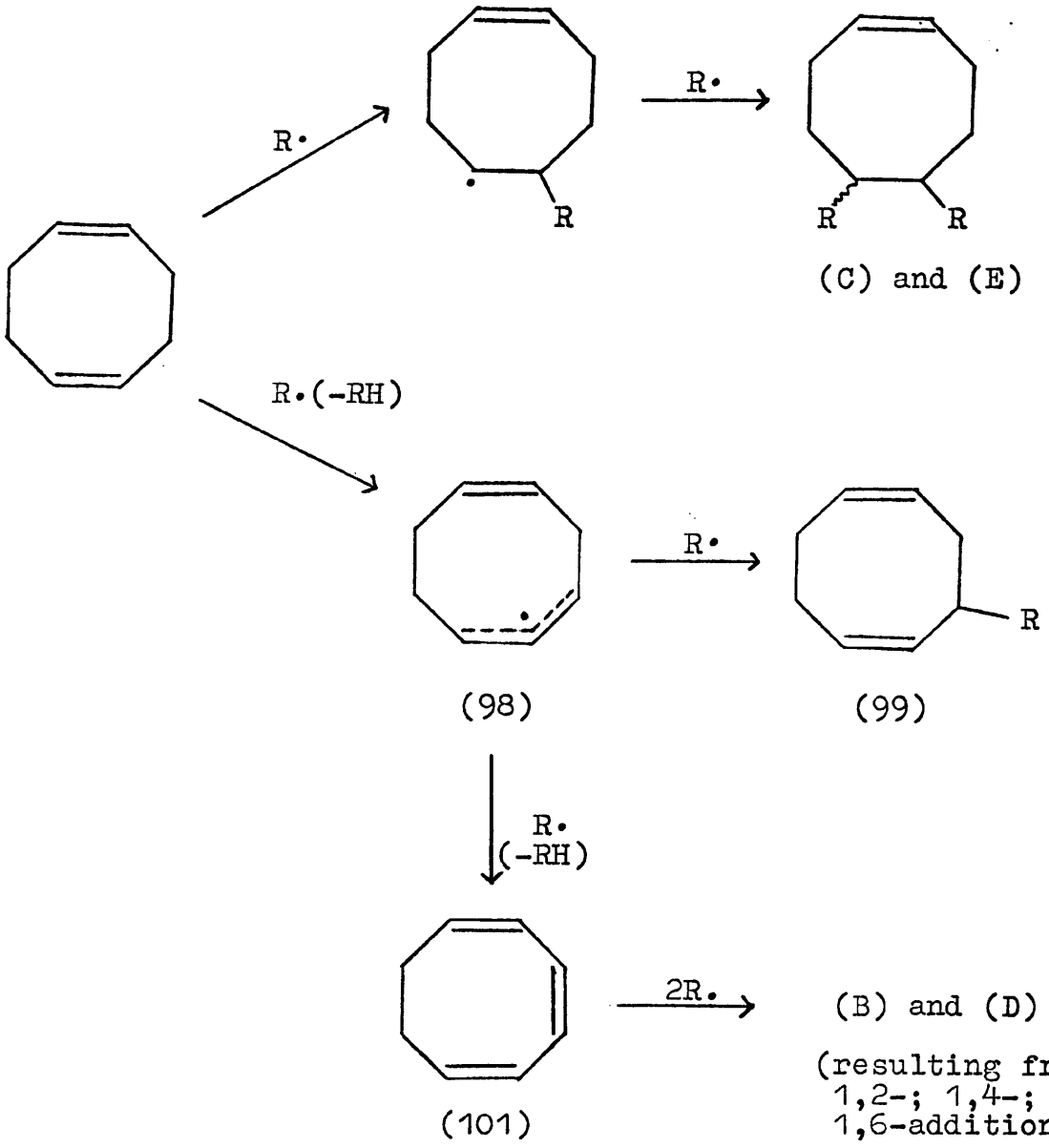
obtained in the cyclo-octa-1,5-diene reaction for the formation of two disubstituted cyclo-octene derivatives (in the ratio ca. 1:1), indicating that in this case anti-addition of (6) was not favoured over syn-addition.

Alternatively, the oxyl (6) can abstract a hydrogen atom to form the allylic radical intermediate (98), which may then be either directly scavenged by (6) to give the monosubstituted cyclo-octadiene derivative (99) [or (100)], or suffer further hydrogen abstraction to give the conjugated cyclo-octatriene (101) which is then quickly scavenged by (6); although several disubstituted isomers are possible, only two were formed, and it was not possible to identify them.

A related reaction is that between the oxyl (6) and cyclopentene[83] which affords bis(amino-oxy)cyclopentenes, i.e.



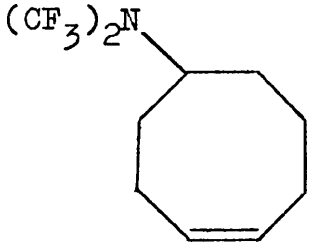
Reaction of the oxyl (6) with cyclo-octa-1,5-diene



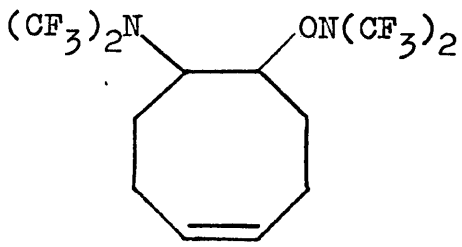
Scheme 15.

(ii) Reaction of the oxadiazapentane (7) with cyclo-octa-1,5-diene

The reaction of an equimolar mixture of the oxadiazapentane (7) with the diene at room temperature (6d) gave NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, unchanged cyclo-octadiene (10% recovered), an unidentified monosubstituted amino-oxy-cyclo-octadiene (A) (ca. 13% based on consumed diene), a product tentatively identified as 1-NN-bistrifluoromethylaminocyclo-oct-5-ene (102) (ca. 9% based on consumed diene), and two diastereoisomers of 1-NN-bistrifluoromethylamino-2(NN-bistrifluoromethylamino-oxy)cyclo-oct-5-ene (103) (34% and 28% respectively, based on consumed diene).



(102)



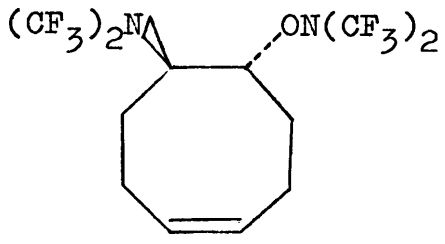
(103)

The two diastereoisomers of compound (103) were identified by elemental analysis and the spectroscopic data outlined below.

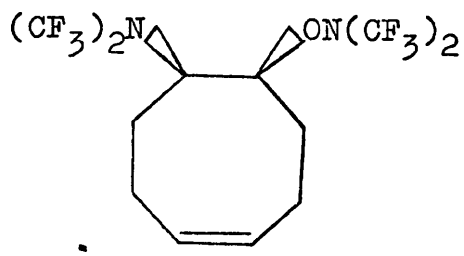
The ^1H n.m.r. spectra of the two diastereoisomers were poorly resolved and were of little help in determining which of the two products was the trans-isomer and which was the cis-isomer; each showed broad complex absorptions in the

regions δ ca. 1.2-2.5 (8H), ca. 3.6-4.3 (2H), and ca. 5.5 (2H) p.p.m., as expected for methylene protons, the protons in $>CHON(CF_3)_2$ and $>CHN(CF_3)_2$ groups, and olefinic protons, respectively.

The ^{19}F n.m.r. spectrum of the major diastereoisomer (1) showed absorptions at δ 27.9 (-9.3) (c) and 15.7 (-21.6) (s) p.p.m., integrated intensities 1:1, assigned to the fluorines in $(CF_3)_2NOCH$ and $(CF_3)_2NCH$ groups, respectively. The ^{19}F n.m.r. spectrum of diastereoisomer (2) showed (i) a broad singlet at δ 28.0 (-9.2) p.p.m., and (ii) broad complex absorptions at δ ca. 18.7 (-18.6) p.p.m. and δ ca. 11.9 (-25.4) p.p.m., integrated intensities 2: 1: 1, assigned to fluorines in a $(CF_3)_2NOCH$ group, and non-equivalent CF_3 groups in a $(CF_3)_2NCH$ group, respectively. It is considered that diastereoisomer (1) is the trans-adduct (103a), where the bulky $(CF_3)_2N$ and $(CF_3)_2NO$ groups are anti- to each other, and that diastereoisomer (2) is the cis-adduct (103b) resulting from syn-addition, i.e.



(103a)



(103b)

The greater hindrance towards rotation of the CF_3 groups in the $(CF_3)_2NCH$ group of the cis-isomer results in the non-equivalence as seen in the ^{19}F n.m.r. spectrum.

The i.r. spectrum of diastereoisomer (1) showed absorptions at 3.29-3.46 (C-H str.), 5.87 and 6.07 (C:C str.), 6.94-8.70 (C-F str.), 9.69 (C-O-N str.), 10.36 (C-N str.), and 14.08 (CF_3 def.)μm, while that of diastereoisomer (2) showed absorptions at 3.31-3.48 (C-H str.), 5.87 and 6.05 (C:C str.), 6.97-8.70 (C-F str.), 9.62 (C-O-N str.), 10.33 (C-N str.), and 14.03 (CF_3 def.)μm.

The mass spectra of the two isomers were very similar and showed peaks at m/e 276 {2%, $[M-(CF_3)_2N]^+$}, 260 {16%, $[M-(CF_3)_2NO]^+$}, 124 (7%, $C_8H_{12}O^+$), 108 (6%, $C_8H_{12}^+$), 81 (100%, $C_5H_5O^+/C_6H_9^+$), and 69 (49%, CF_3^+).

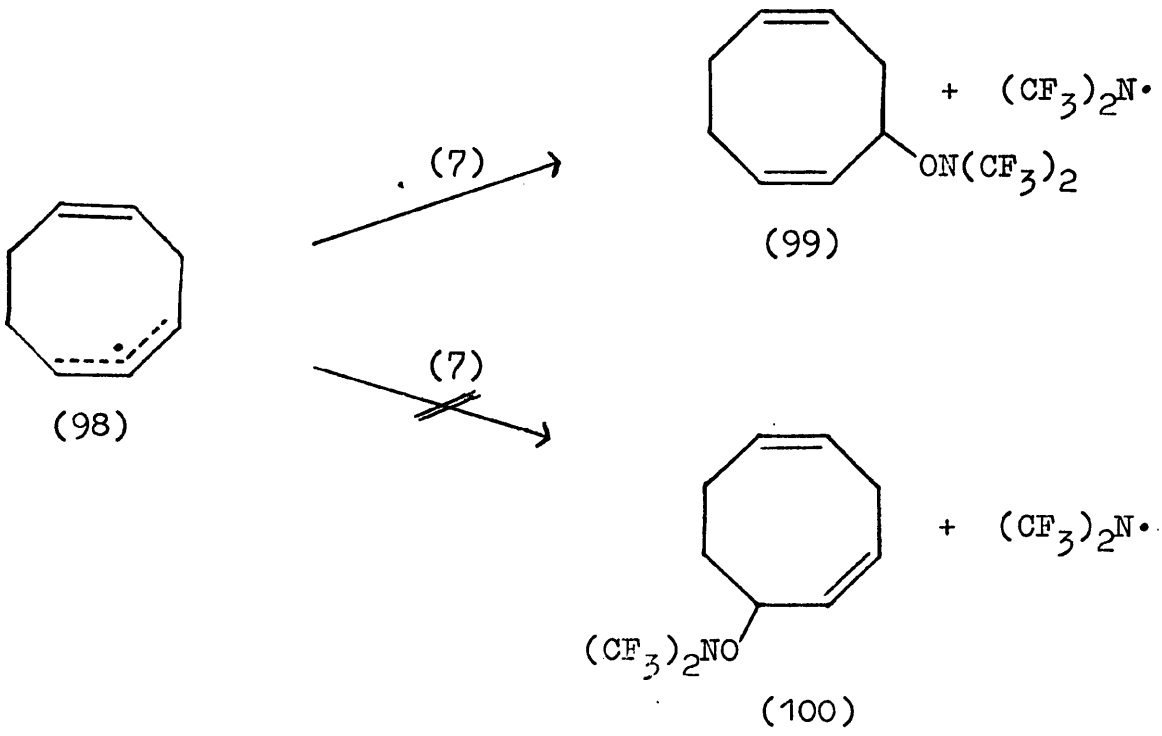
The i.r. and mass spectra of the monosubstituted product (A) were not recorded as insufficient sample was isolated.

The ^1H n.m.r. spectrum showed complex absorptions in the regions δ ca. 1.2-2.6 (6H), ca. 5.05 (1H), and ca. 5.5 (4H) p.p.m., assigned to methylene protons, a $>CHON(CF_3)_2$ group, and olefinic protons, respectively, while a singlet absorption was observed in the ^{19}F n.m.r. spectrum at δ 27.0 (-10.3) p.p.m., typical of the fluorines in an amino-oxy group.

The g.l.c. retention time of compound (A) was identical to that of the monosubstituted product obtained in the reaction of the oxyl (6) with cyclo-octa-1,5-diene (p. 137). However, the n.m.r. spectra of the two compounds were very poorly resolved and were not sufficiently clear to allow a

direct comparison to be made of the two spectra.

It is considered, however, that as suggested for the oxyl reaction, chain-transfer of the allylic intermediate (98) with the oxadiazapentane (7) is predominantly at the 4-position, to give the relatively less strained cyclo-octa-1,5-diene derivative (99), i.e.



The i.r. and mass spectra of the amino-substituted cyclo-octene derivative (102) were not recorded as only a small amount of contaminated material was isolated.

The ^1H n.m.r. spectrum was poorly resolved and showed broad complex absorptions at δ ca. 1.2-2.6, ca. 3.1-3.7, and ca. 5.7 p.p.m., as expected for methylene protons, a $>CHN(CF_3)_2$ group, and olefinic protons, respectively. The relative intensities of the absorptions were rather unclear

due to the poor resolution of the spectrum. Nevertheless, the relative intensities of the olefinic absorption and the $>CHN(CF_3)_2$ group absorption were closer to 2:1 rather than 4:1 as would be expected for a cyclo-octadiene derivative.

The ^{19}F n.m.r. spectrum showed a singlet absorption at δ 14.15 (-23.1) p.p.m., assigned to the fluorines in a $(CF_3)_2N$ group.

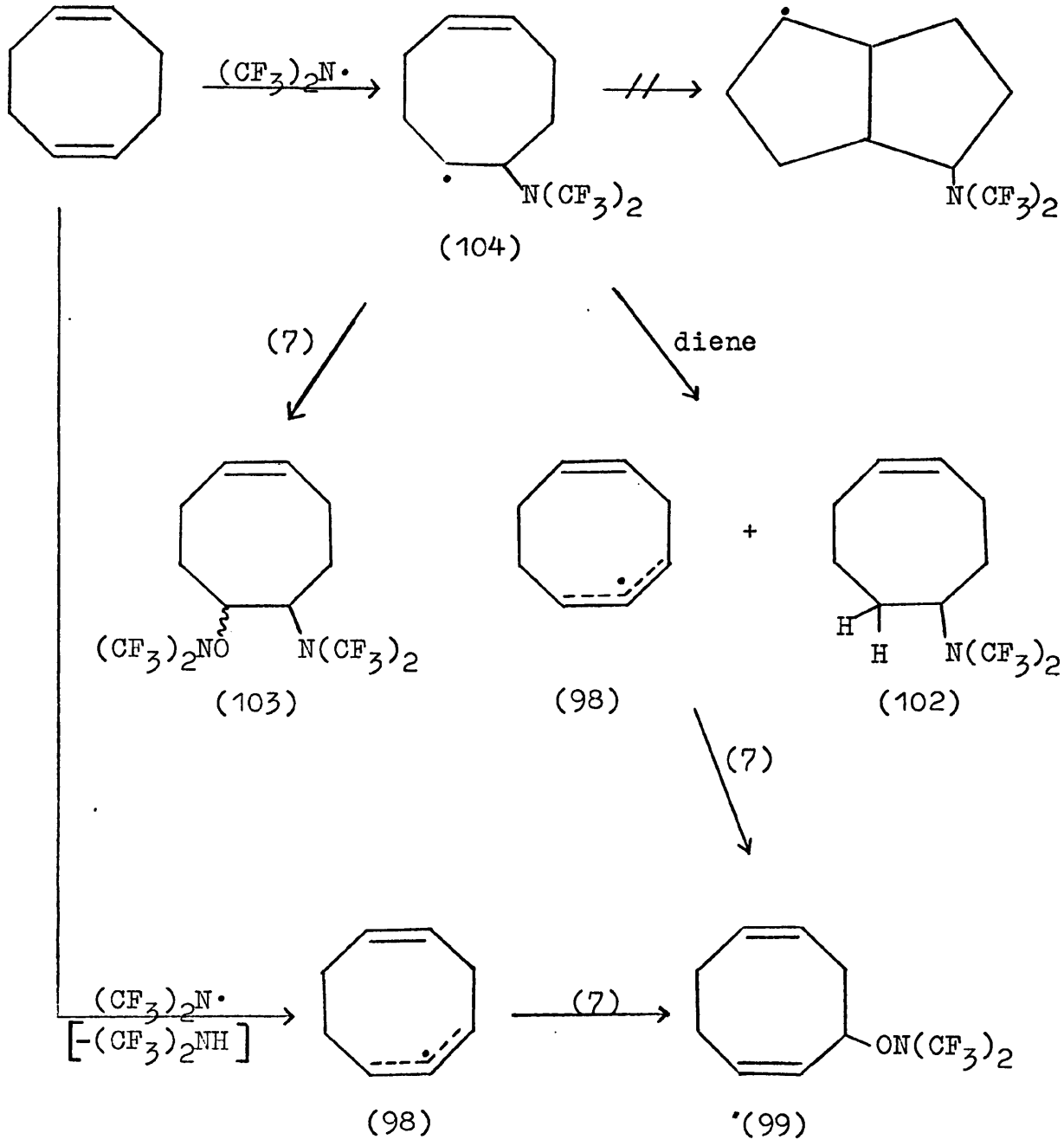
The formation of the products may be explained by the mechanism outlined in Scheme 16.

Although the monosubstituted amino-oxy derivative (99) was only obtained in low yield (ca. 13%), the amounts of the lower-boiling products (NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine) indicated that considerable hydrogen abstraction had occurred.

The slow rate of chain-transfer of the intermediate cyclo-octyl radical (104) with the oxadiazapentane (7) results in competition between formation of the addition products (103a) and (103b), and abstraction of hydrogen by the cyclo-octyl radical intermediate (104) from the starting material to form the bistrifluoromethylamino-substituted cyclo-octene (102) [cf. reaction of (7) with 2(10)-pinene (p. 120)].

The identified products were formed in reasonable yield (ca. 84%) and thus rearrangement of the intermediate cyclo-octyl radical (104) was not favoured although cyclisation would perhaps have been expected since the oxadiazapentane (7) is not recognised as an efficient chain-transfer agent.

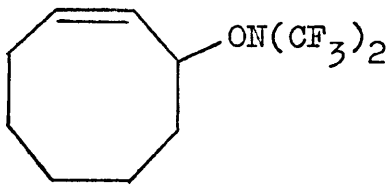
Reaction of the oxadiazapentane (7) with cyclo-octa-1,5-diene



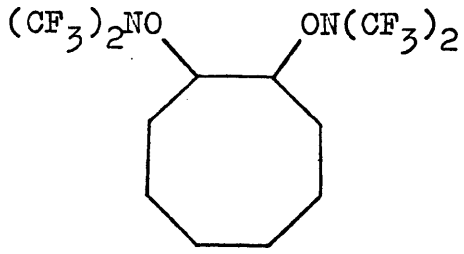
Scheme 16

(b) The reaction of the oxyl (6) with cyclo-octene

The reaction of a 2:1 molar mixture of the oxyl (6) and cyclo-octene reached completion on warming from -196 °C to room temperature and gave NN-bistrifluoromethylhydroxylamine [10% based on (6)], unchanged olefin (18% recovered), three minor unidentified products, 3-(NN-bistrifluoromethylamino-oxy)cyclo-oct-1-ene (105) (20% based on consumed olefin), and 1,2-bis(NN-bistrifluoromethylamino-oxy)cyclo-octane (106) (67.5% based on consumed olefin).



(105)



(106)

The two isolated amino-oxy derivatives were identified by elemental analysis and spectroscopic data.

3-(NN-bistrifluoromethylamino-oxy)cyclo-oct-1-ene (105)

The i.r. spectrum showed the characteristic absorptions of an amino-oxy group together with bands at 3.30-3.50 (C-H str.) and 6.06 (C:C str.) μm.

The ^{1}H n.m.r. spectrum showed (i) broad complex absorptions at δ ca. 1.35 (6H) and 1.9 (4H) p.p.m., assigned to the methylene protons [the lower-field signal probably being due to the protons adjacent to the olefinic and $>CHON(CF_3)_2$ groups], and (ii) multiplets at δ ca. 4.73 (1H)

and 5.4 (2H) p.p.m., assigned to the methine proton in a $>CHON(CF_3)_2$ group, and the olefinic protons, respectively.

The ^{19}F n.m.r. spectrum showed a broad absorption at δ 28.4 (-8.8) p.p.m., typical of the fluorines in an amino-oxy group.

The mass spectrum showed peaks at m/e 277 (1%, M^+), 276 [2%, $(M-H)^+$], 125 (1%, $C_8H_{13}O^+$), 109 (55%, $C_8H_{13}^+$), and 67 (100%, $C_5H_7^+$).

1,2-Bis(NN-bistrifluoromethylamino-oxy)cyclo-octane (106)

The i.r. spectrum showed only that it was an amino-oxy-substituted alkane.

The ^1H n.m.r. spectrum showed (i) broad absorptions at δ ca. 1.4 (8H) and ca. 1.75 (4H) p.p.m., assigned to the methylene ring protons [the lower-field signal probably being due to the protons adjacent to the $>CHON(CF_3)_2$ groups], and (ii) complex signals at δ 4.05 (1H) and 4.18 (1H) p.p.m., assigned to the protons in the non-equivalent $>CHON(CF_3)_2$ groups, respectively.

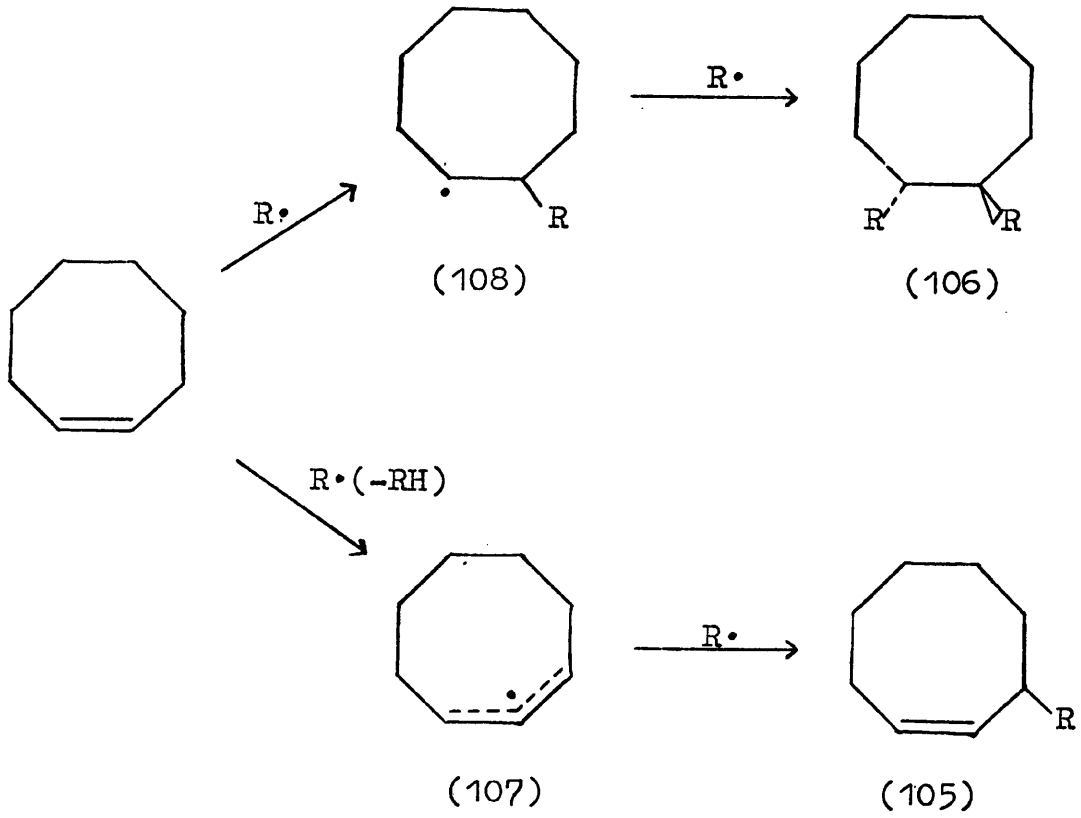
The ^{19}F n.m.r. spectrum showed absorptions at δ 28.5 (-8.7) (s) and 28.25 (-9.0) (bs) p.p.m., integrated intensities 1:1, assigned to the fluorines in the two amino-oxy groups.

The mass spectrum showed peaks at m/e 278 {1.5%, $[M-(CF_3)_2NO]^+$}, 126 (5.5%, $C_8H_{14}O^+$), 110 (9%, $C_8H_{14}^+$), and 109 (100%, $C_8H_{13}^+$).

The formation of the products may be explained by the mechanism outlined in Scheme 17.

While the reaction of the oxyl (6) with C_5-C_7 cyclo-

alkenes has been reported[83] to give monosubstituted amino-oxy derivatives as the major products (66-93%), via allylic hydrogen abstraction, the reaction with cyclo-octene gives the adduct (106) as the major product. It is suggested that due to the ring strain in cyclo-octene, ring skewing is very acute and results in poor stabilisation of the cyclo-octenyl radical intermediate (107).



Scheme 17

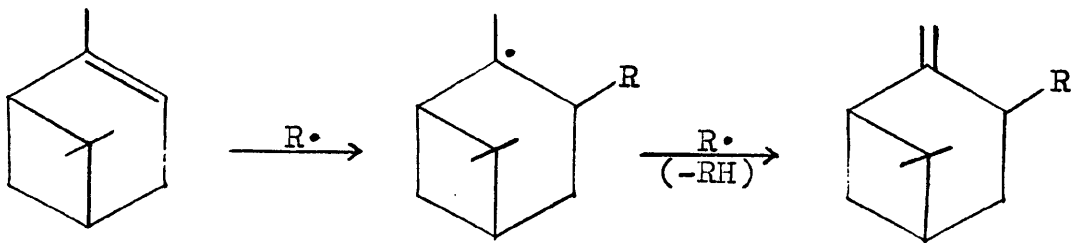
The transannular 1,5-shift of hydrogen is believed to involve an energy of activation of ca. 18-19 Kcal/mol and is poorly competitive with scavenging by (6) [to give the adduct (106)] under the conditions used in this reaction.

Only one disubstituted adduct was isolated from the reaction mixture and although it was not possible to unequivocally determine whether it was the trans- or cis-isomer from a consideration of its n.m.r. spectra, it is considered that the trans- configuration is the more likely, as anti-addition will involve the least steric crowding and have more favourable dipole-dipole interactions.

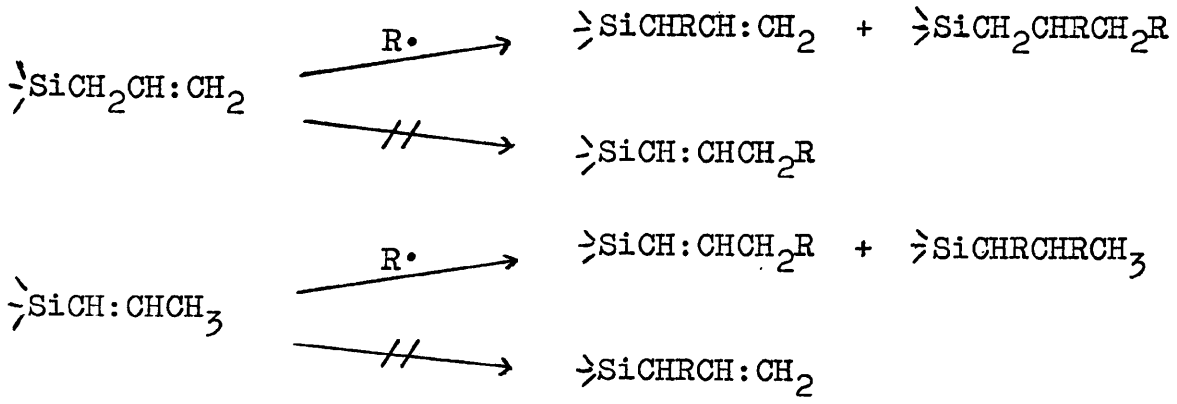
Previous work in this department involving the reactions of the oxyl (6) with C_4-C_7 cyclo-alkenes [83] has shown that disubstituted trans- and cis-adducts were formed in the ratio ca. 3:1, with the exception of cyclo-pentene which gave a relatively higher ratio (ca. 10:1). As the identified products represent a high yield (87%), syn-addition of the oxyl (6) to cyclo-octene to give the cis-isomer must at best be only a minor reaction, probably due to steric interactions between the ring hydrogens in the cyclo-octyl intermediate (108) and the approaching oxyl radical.

D. Allylic migration

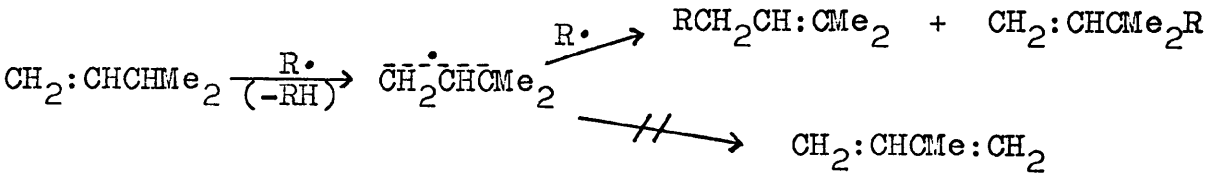
The monosubstituted products formed in the reactions of the oxyl (6) with 2- and 2(10)-pinene indicated that complete allylic migration had occurred, since only one isomer was formed in each case, and it is postulated that this probably occurred via an addition/disproportionation mechanism, i.e.



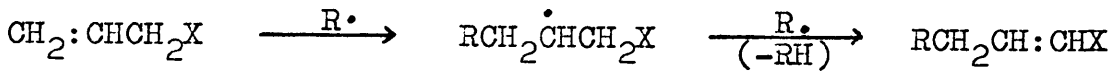
In contrast, previous work in this department has shown that in the reaction of the oxyl (6) with certain alkenylsilanes allylic migration did not occur,[114] e.g.



However, in the reaction of the oxyl (6) with 3-methylbut-1-ene it was found that both the 1- and 3-amino-oxy-substituted isomers were formed, and that no disproportionation occurred,[82] i.e.

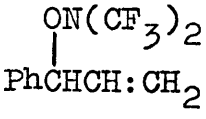


Hence, the reactions of allylbenzene and penta-1,4-diene with the oxyl (6), and also with the oxadiazapentane (7) (as a comparison) were investigated. If an addition/disproportionation mechanism took place then hydrogen abstraction from the intermediate radical should be favoured by the formation of a conjugated olefin, resulting in the exclusive formation of the terminal isomer, i.e. (where X= CH_2:CH and Ph)

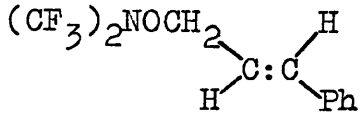


(a) (i) The reaction of the oxyl (6) with allylbenzene

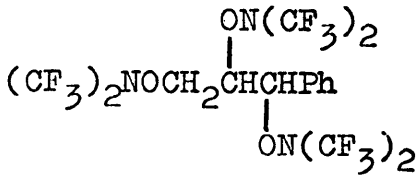
A 2.5:1 molar mixture of the oxyl (6) and allylbenzene reacted on warming from -196 °C to room temperature to afford NN-bistrifluoromethylamine [ca. 2.5% based on (6)], NN-bistrifluoromethylhydroxylamine (32% based on oxyl), unchanged allylbenzene (17% recovered), 3-(NN-bistrifluoromethylamino-oxy)-3-phenylpropene (109) (37% based on consumed olefin), trans-3-(NN-bistrifluoromethylamino-oxy)-1-phenylpropene (110) (16.5% based on consumed olefin), two diastereoisomers of 1,2,3-tri(NN-bistrifluoromethylamino-oxy)-3-phenylpropane (111a) (20.5%) and (111b) (10% based on consumed olefin), and four minor unidentified products.



(109)



(110)



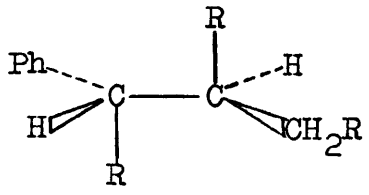
(111)

The reaction was repeated using a 4.3:1 molar ratio of the oxyl (6) and allylbenzene at room temperature (20min) and this gave NN-bistrifluoromethylhydroxylamine (28% based on oxyl), perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (7) (ca. 2% based on oxyl), (109) (24%), (111a) (45.5%) and (111b) (21% based on olefin), and three minor unidentified products including one (A) which was not detected in the first reaction. The monosubstituted propene (110) was not detected in the products of this second reaction.

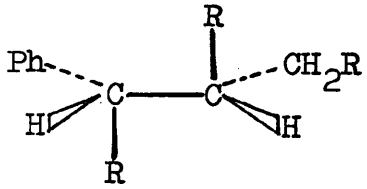
The amino-oxy-substituted products (109), (110), and (111a) were identified by elemental analysis and spectral data

while the minor trisubstituted product (111b) was identified by a consideration of its n.m.r. and mass spectra.

The 1,2,3-trisubstituted products (111a) and (111b) were formed in each case in the ratio ca. 2:1, and it is suggested that the major diastereoisomer (111a) is the anti-adduct, i.e. the erythro-isomer, and the minor isomer (111b) is the syn-adduct, i.e. the threo-isomer. The preferred conformations of these isomers are probably those in which the bulky $(CF_3)_2NO$ groups are anti- to each other, i.e. [where R= $(CF_3)_2NO$]



(111a)

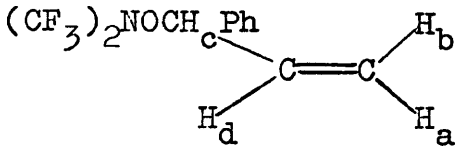


(111b)

3-(NN-bistrifluoromethylamino-oxy)-3-phenylpropene (109)

The i.r. spectrum showed absorptions at 3.24-3.42 (C-H str.), 6.10-7.03 (C:C str.), 13.12 and 14.33 (C-H def.)μm, together with absorptions characteristic of an amino-oxy group at 7.71-8.33 (C-F str.), 9.67 (C-O-N str.), 10.40 (C-N str.), and 14.10 (CF_3 def.)μm.

The ^1H n.m.r. spectrum showed absorptions at δ ca. 4.6 (1H, c, H_a) ca. 4.75 (2H, c, H_b and H_c), ca. 5.5 (1H, m, H_d), and 6.66 (5H, c, C_6H_5) p.p.m.



The ^{19}F n.m.r. spectrum showed a complex absorption at δ 28.0 (-9.3) p.p.m., typical of fluorines in an amino-oxy group bound to an asymmetric carbon.

The mass spectrum showed peaks at m/e 285 (1%, M^+), 117 (100%, $C_9H_9^+$), 103 (3%, $C_8H_7^+$), 91 (16%, $C_7H_7^+$), and 77 (8.5%, $C_6H_5^+$).

Trans-3-(NN-bistrifluoromethylamino-oxy)-1-phenylpropene (110)

The i.r. spectrum showed absorptions at 3.24-3.45 (C-H str.), 6.04-6.35 and 6.69-6.90 (C:C str.), 7.72-8.30 (C-F str.), 9.62 (C-O-N str.), 10.34 (C-N str.), 13.36 and 14.45 (C-H def.), and 14.08 (CF_3 def.)μm

The ^1H n.m.r. spectrum showed absorptions at δ 3.92 (2H, d, J= 7Hz), 5.44 (1H, ABt, J= 15Hz, 7Hz), 5.80 (1H, AB, J= 15Hz), and 6.58 (5H, bs) p.p.m., assigned to protons in a $-CH_2ON(CF_3)_2$ group, two non-equivalent olefinic protons, and a phenyl group, respectively. The ^{19}F n.m.r. spectrum showed a singlet at δ 29.0 (-8.3) p.p.m., assigned to fluorines in an amino-oxy group.

The fragmentation pattern in the mass spectrum was virtually identical to that of compound (109).

Erythro-1,2,3-tri(NN-bistrifluoromethylamino-oxy)-3-phenylpropane (111a)

The i.r. spectrum showed very strong amino-oxy group absorptions and weak absorptions at 3.26-3.37 (C-H str.), 6.22-6.89 (C:C ring str.), and 12.45-14.53 (C-H def.)μm.

The ^1H n.m.r. spectrum showed (i) a poorly resolved ABd system centred on δ ca. 3.95 p.p.m., (ii) complex absorptions at δ ca. 4.46 and 4.9 p.p.m., and (iii) a broad singlet at

δ 6.95 p.p.m., integrated intensities 2: 1: 1: 5, assigned to protons in the groups $-CH_2ON(CF_3)_2$, $>CHON(CF_3)_2$, $CHPhON(CF_3)_2$, and phenyl, respectively. The ^{19}F n.m.r. spectrum showed a singlet at δ 30.0 (-7.25) p.p.m., and two overlapping broadened singlets at δ 28.95 (-8.8) and 28.9 (-8.4) p.p.m., integrated intensities 1:1:1 assigned to the $-CH_2ON(CF_3)_2$ and the two more hindered $>CHON(CF_3)_2$ groups, respectively.

The mass spectrum showed peaks at m/e 453 {1.5%, $[M-(CF_3)_2NO]^+$}, 285 (2%, $C_{11}H_9F_6NO^+$), 258 (20%, $C_9H_6F_6NO^+$), 182 [2%, $(CF_3)_2NOCH_2^+$], 117 (100%, $C_9H_9^+$), 91 (78%, $C_7H_7^+$), and 77 (23%, $C_6H_5^+$).

Threo-1,2,3-tri(NN-bistrifluoromethylamino-oxy)-3-phenylpropane (111b)

The ^1H n.m.r. spectrum showed absorptions at δ ca. 3.6 (1H, c), ca. 4.0 (1H, c), ca. 4.34 (1H, c), ca. 4.85 (1H, poorly resolved doublet), and 6.97 (5H, bs) p.p.m., assigned to two non-equivalent methylene protons in a $-CH_2ON(CF_3)_2$ group, and the protons in $>CHON(CF_3)_2$, $-CHPhON(CF_3)_2$ and phenyl groups, respectively. The spectrum was very similar in appearance to that of the erythro-isomer, but more poorly resolved.

The ^{19}F n.m.r. spectrum showed two broad absorptions at δ 29.7 (-7.55) and 28.65 (-8.65) p.p.m., integrated intensities 1:2, assigned to fluorines in a $(CF_3)_2NOCH_2$ and $>CHON(CF_3)_2$ groups, respectively.

Confirmation of the structure was obtained from the mass spectrum which showed a fragmentation pattern virtually

identical to that of the erythro-isomer (111a).

Although the reaction of allylbenzene with N-bromosuccinimide[115,116] and trichlorobromomethane[117,118] have been reported to give only the terminal monosubstituted isomers, the 3-amino-oxy-substituted isomer (109) was isolated in reasonable yield and this confirms the intermediacy of an allylic radical intermediate (112) [Scheme 18; where R= $(CF_3)_2NO$]. Since the addition product (113) was not detected, initial attack of the oxyl (6) is apparently virtually exclusively via hydrogen abstraction to give the resonance-stabilised allylic intermediate (112), which is then scavenged at both the 1- and 3-positions to give the monosubstituted products (109) and (110). Both isomers may then undergo further attack by the oxyl (6) to give the trisubstituted products (111a) and (111b). It appears, however, that the 1-substituted isomer (110) is the more reactive, as this compound was not detected when a larger excess of oxyl was used. The greater reactivity of this isomer is due to the fact that further attack of the oxyl generates a benzylic radical, i.e.

$$\underset{(110)}{PhCH{:}CHCH_2R} \xrightarrow{R\cdot} PhCHCHRCH_2R \xrightarrow{R\cdot} (111)$$

Only the trans-1-substituted isomer was isolated from the reaction mixture and it is possible that cis-1-(NN-bis-trifluoromethylamino-oxy)-3-phenylpropene (114) was also formed initially but that it was scavenged completely by the oxyl.

Although several minor products remain unidentified, the identified products represent a high yield (84 and 90% respectively), and so direct addition of (6) to the double bond of allylbenzene is at best only a minor reaction; it is considered unlikely that any 1,2-bis(amino-oxy) adduct (113) so formed would undergo further reaction [to give compounds (111 a) and (111 b)] due to the presence of the two bulky amino-oxy groups.

The i.r. spectrum of the higher-boiling mixture in the second reaction (4.3:1 molar ratio) showed a weak absorption in the region 5.81-6.01 (C:O str.)μm, not present in the first reaction mixture, and this coupled with the formation of the oxadiazapentane (7) indicates that the new product (A) (detected by g.l.c.) was an ester-type product, resulting from further attack of (6) on a $-CH_2ON(CF_3)_2$ group, e.g.

$$PhCH{:}CHCH_2R \xrightarrow[(-RH)]{R\bullet} PhCH{:}C\dot{H}CHR$$

(110)

$$PhCH{:}C\dot{H}CHR \xrightarrow{R\bullet} PhCH{:}CHCHR_2$$

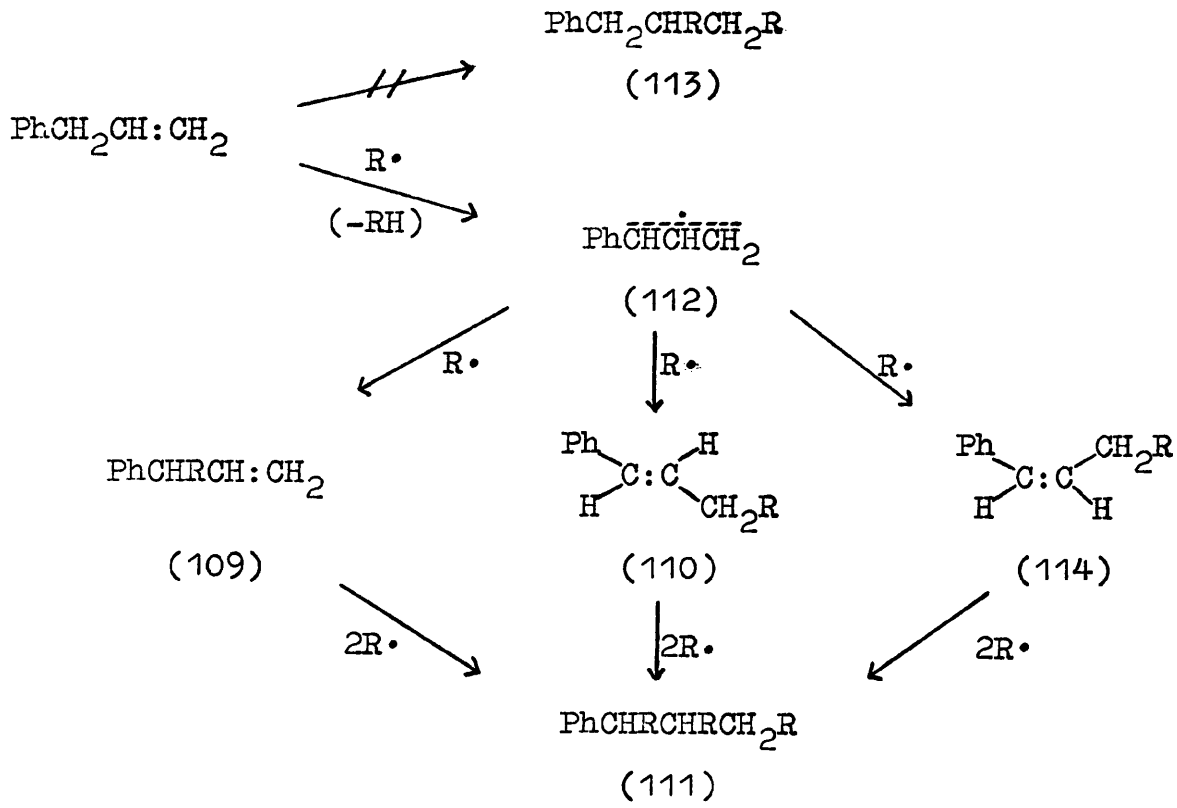
$$PhCH{:}CHCHR_2 \longrightarrow PhCH{:}CHCHO \xrightarrow[(-RH)]{R\bullet} \xrightarrow{R\bullet} PhCH{:}CHCRO$$

(A)

$$+ \quad (CF_3)_2NON(CF_3)_2$$

(7)

Reaction of the oxyl (6) with allylbenzene



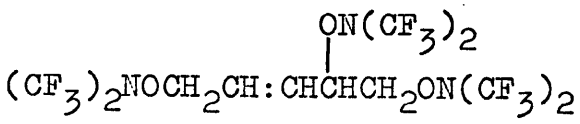
Scheme 18

(ii) With penta-1,4-diene

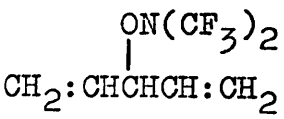
A 2:1 molar mixture of the oxyl (6) and penta-1,4-diene on reaction at -78 °C (30min) gave NN-bistrifluoromethylhydroxylamine (ca. 30% based on oxyl), unchanged diene (ca. 44% recovered), 1,2,5-tri(NN-bistrifluoromethylamino-oxy)-pent-3-ene (115) (44.5% based on consumed diene), 3-(NN-bistrifluoromethylamino-oxy)penta-1,4-diene (116) (26.5% based on diene), two products tentatively identified as 1-(NN-bistrifluoromethylamino-oxy)penta-2,4-diene (117) (ca. 19% based on diene), and 1,2-bis(NN-bistrifluoromethylamino-oxy)pent-4-ene (118) (ca. 2.5% based on diene), and an unidentified

trisubstituted product (A) (ca. 5% based on diene).

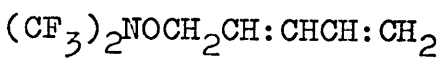
The reaction was repeated in the gas phase at room temperature, again using a 2:1 molar mixture of reactants, and this gave a virtually identical product ratio.



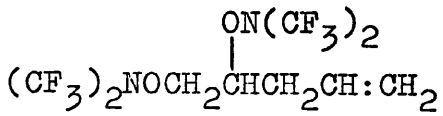
(115)



(116)



(117)



(118)

The trisubstituted product (115) was identified by elemental analysis and spectroscopic data. The coupled g.l.c./mass spectrum of product (A) was identical to that of compound (115).

The monosubstituted product (116) was isolated contaminated with NN-bistrifluoromethylhydroxylamine and was identified by a consideration of the n.m.r. spectra of the two-component mixture, and by its coupled g.l.c./mass spectrum. The coupled g.l.c./mass spectrum of product (117) was identical to that of the 3-substituted product (116).

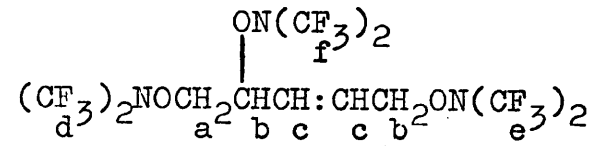
The disubstituted product (118) was tentatively identified on the basis of its coupled g.l.c./mass spectrum.

1,2,5-Tri(NN-bistrifluoromethylamino-oxy)pent-3-ene (115)

The i.r. spectrum showed absorptions at 3.31-3.47 (C-H str.), 5.89 and 5.98 (C:C str.), 7.72-8.33 (C-F str.), 9.40 and/or 9.57 (C-O-N str.), 10.37 (C-N str.), and 14.10 (CF_3

def.)μm.

The ^{1}H n.m.r. spectrum showed absorptions at δ 3.84 (2H, d, J= 5Hz), ca. 4.2 (3H, c), and ca. 5.51 (2H, m) p.p.m., which were assigned to H_a, H_b, and H_c, respectively. The ^{19}F n.m.r. spectrum showed singlet absorptions at δ 30.2 (-7.1) and 29.9 (-7.4), and a broad complex signal at ca. 29.2 (-8.1) p.p.m., integrated intensities 1: 1: 1, which were assigned to F_d, F_e, and F_f, respectively.

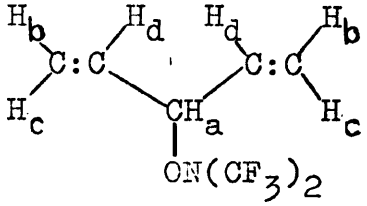


The mass spectrum showed peaks at m/e 552 [1%, $(M-F)^+$], 403 {13%, $[M-(CF_3)_2NO]^+$}, 234 (6%, $C_7H_6F_6NO^+$), 221 (2%, $C_6H_5F_6NO^+$), 182 [7%, $(CF_3)_2NOCH_2^+$], 83 (6%, $C_5H_7O^+$), and 67 (54%, $C_5H_7^+$).

3-(NN-bistrifluoromethylamino-oxy)penta-1,4-diene (116)

The ^{1}H n.m.r. spectrum showed absorptions at δ 4.33 (1H, t, J= 7Hz), 4.78 (2H, c), 4.92 (2H, d, J= 3Hz), and ca. 5.4 (2H, m) p.p.m., assigned to H_a, H_b, H_c, and H_d, respectively.

The ^{19}F n.m.r. spectrum showed a singlet at δ 29.0 (-8.3) p.p.m., which was assigned to the fluorines in an amino-oxy group.



The mass spectrum showed peaks at m/e 235 (1%, M^+), 68

(6%, $C_4H_4O^+$), 67 (100%, $C_5H_7^+$), and 41 (33%, $C_3H_5^+$).

1,2-Bis(NN-bistrifluoromethylamino-oxy)pent-4-ene (118)

The mass spectrum showed peaks at m/e 403 [6%, $(M-H)^+$], 363 [1%, $(M-C_3H_5)^+$], 208 (23%, $C_5H_4F_6NO^+$), 182 [14%, $(CF_3)_2NOCH_2^+$], 82 (12%, $C_5H_6O^+$), 68 (5%, $C_4H_4O^+/C_5H_8^+$), 67 (29%, $C_5H_7^+$), and 41 (35%, $C_3H_5^+$).

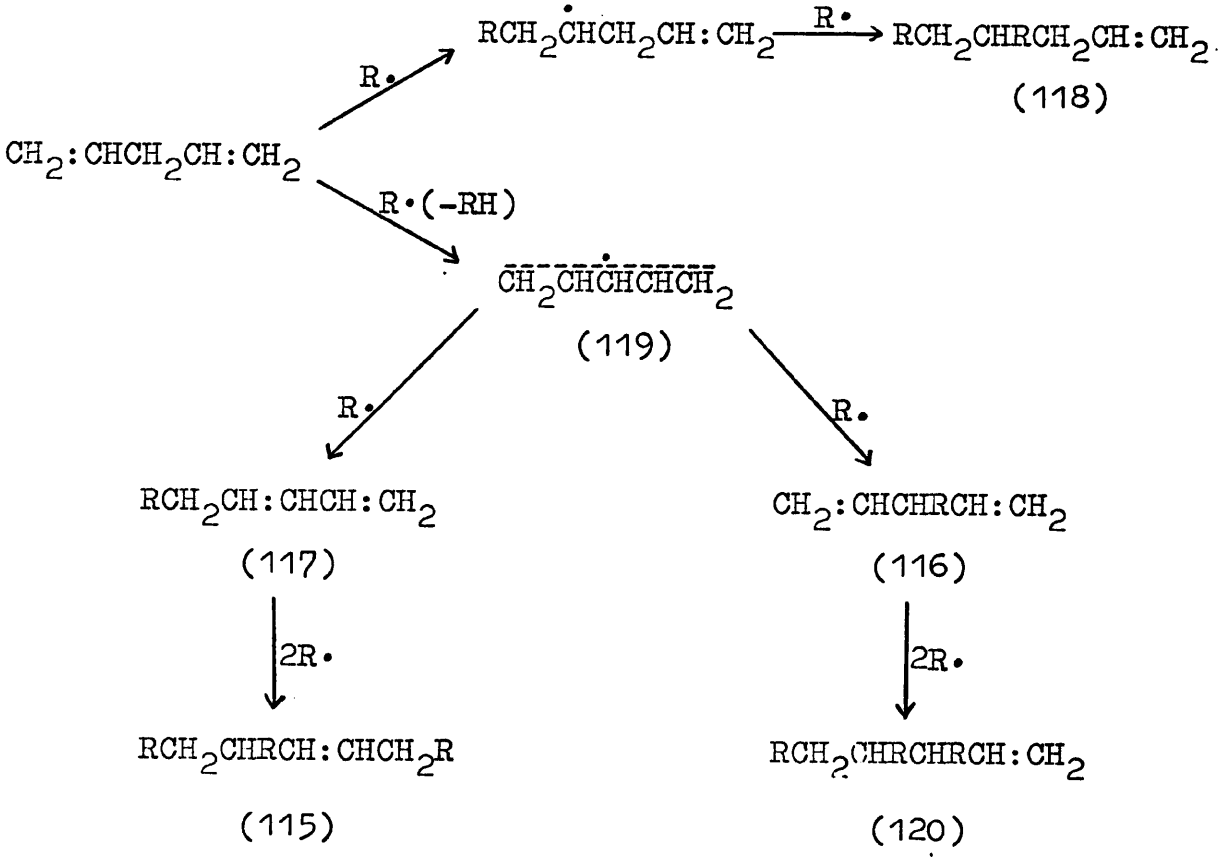
The formation of the products may be explained by the mechanism outlined in Scheme 19 [where R= $(CF_3)_2NO$]. An alternative mechanism, involving addition to the double bond followed by hydrogen abstraction, may be discounted, as both the 1- and 3-substituted isomers were detected in the products, indicating that the intermediate is a classical allylic radical (119).

The initial attack of the oxyl (6) is apparently virtually exclusively via hydrogen abstraction, with only a very small amount of addition [to give the disubstituted compound (118)]. The resultant intermediate (119) is then scavenged by (6) at both the 1- and 3- positions to give the products (116) and (117). The conjugated diene (117) can then undergo further attack by (6) via either 1,2- or 1,4-addition to give the trisubstituted product (115). It was not possible to determine from the n.m.r. spectrum of product (115) whether it was the cis- or trans-isomer, but it is most probable that it is the trans-isomer, as the cis-isomer would be subject to considerable steric crowding.

The minor trisubstituted product (A) is possibly the cis-isomer of compound (115), but it is more probable that it is compound (120) arising from further attack of the oxyl (6)

on compound (116).

Reaction of the oxyl (6) with penta-1,4-diene



Scheme 19

(b) (i) The reaction of the oxadiazapentane (7) with allylbenzene

An equimolar mixture of the oxadiazapentane (7) and allylbenzene on reaction at room temperature (6d) gave unchanged (7) (ca. 6% recovered), NN-bistrifluoromethylamine [ca. 5% based on consumed (7)], NN-bistrifluoromethylhydroxylamine [ca. 6% based on consumed (7)], unchanged allylbenzene (ca. 6% recovered), several unidentified products, trans-1-(NN-bistrifluoromethylamino-oxy)-3-phenylpropene (110) (5.5% based on consumed allylbenzene), and 1-NN-bistri-

fluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)-3-phenylpropane (121) (66.5% based on allylbenzene).

$$(CF_3)_2NCH_2\underset{\displaystyle CH_2Ph}{\underset{|}{C}}HON(CF_3)_2$$

(121)

The monosubstituted product (110) has been prepared previously (p. 154) and was identified by g.l.c. analysis. The major product (121) was identified by elemental analysis and the spectroscopic data outlined below.

The i.r. spectrum showed absorptions at 3.22-3.48 (C-H str.), 6.22 and 6.30 (C:C ring str.), 7.22-9.01 (C-F str.), 9.52 (C-O-N str.), 10.34 (C-N str.), and 13.30, 14.04 and 14.25 (CF_3 def. and/or C-H def.) μm.

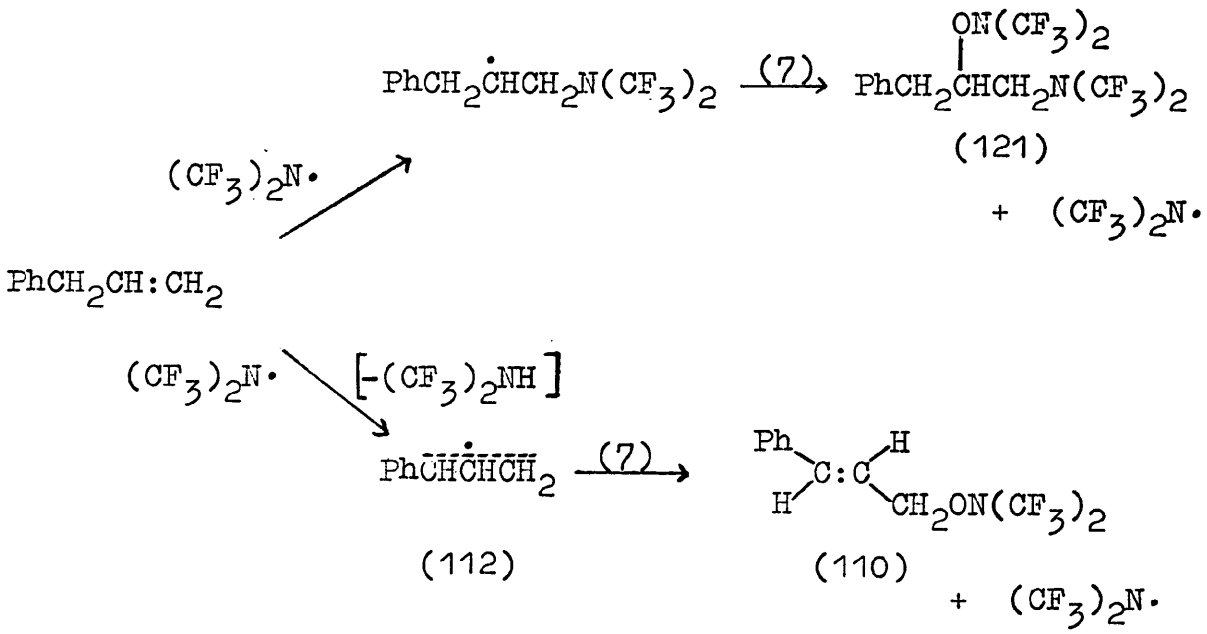
The ^1H n.m.r. spectrum showed absorptions at δ 2.24 (1H, ABd, J= 14Hz, 8Hz), ca. 2.75 (1H, ABd, J= 6Hz), 2.86 (2H, c), 3.99 (1H, c), and ca. 6.75 (5H, c) p.p.m., assigned to two non-equivalent protons in a $-CH_2Ph$ group, and $CH_2N(CF_3)_2$ $>CHON(CF_3)_2$ and Ph protons, respectively.

The ^{19}F n.m.r. spectrum showed absorptions at δ 28.43 (-8.85) (bs) and 18.83 (-18.45) (s) p.p.m., assigned to fluorines in $(CF_3)_2NOCH$ and $(CF_3)_2NCH_2$ groups, respectively.

The mass spectrum showed peaks at m/e 438 (2.5%, M^+), 272 {1%, $[M-(CF_3)_2NCH_2]^+$}, 270 {11.5%, $[M-(CF_3)_2NO]^+$}, 118 (2%, $C_9H_{10}^+$), 117 (10%, $C_9H_9^+$), 91 (100%, $C_7H_7^+$), and 77 (2%, $C_6H_5^+$).

Although several products were not identified, the low yield of NN-bistrifluoromethylamine indicates that hydrogen

abstraction did not occur to any great extent, and, in contrast to the corresponding oxyl reaction, it is apparent that addition to the double bond is the major process, i.e.



The $(CF_3)_2N\cdot$ radical is more reactive than the oxyl (6) and hence it is probable that it is less sensitive to stabilisation afforded to the radical intermediate resulting from hydrogen abstraction. Secondly, it is more electrophilic than the oxyl (6) and thus it is more sensitive to polar effects. As both the Ph and olefin groups are electron-withdrawing, abstraction of the benzylic/allylic hydrogens to give intermediate (112) is less favourable and so the $(CF_3)_2N\cdot$ radical adds mainly to the electron-rich double bond.

The product mixture was rather more complex than expected, and it is possible that some reverse addition occurs as a result of the polarisation of the olefin, i.e.

$$Ph\leftarrow CH_2\overset{\delta-}{-}CH\overset{\delta+}{=}CH_2 + (CF_3)_2\overset{\delta+}{N}\cdot \longrightarrow PhCH_2\underset{\underset{N(CF_3)_2}{|}}{CH}CH_2\cdot \longrightarrow \underline{etc}.$$

Furthermore, the amino-oxy-substituted product (110) may react further with the oxadiazapentane (7) as was found in the corresponding oxyl reaction.

(ii) With penta-1,4-diene

An equimolar mixture of the oxadiazapentane (7) and the diene on reaction in the gas phase at room temperature (2d) gave a very complex mixture of products which contained unchanged diene (ca. 13% recovered), NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, and 1-NN-bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)pent-4-ene (122) (ca. 70% based on consumed diene), which was identified by elemental analysis and the spectroscopic data outlined below.

$$(CF_3)_2NCH_2\underset{\underset{ON(CF_3)_2}{|}}{CH}CH_2CH{:}CH_2$$

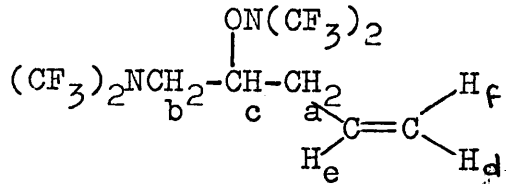
(122)

The reaction was repeated in the liquid phase at room temperature (2d) using a slight excess of (7) and this gave an even more complex mixture of products, including NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, unchanged diene, the adduct (122) (ca. 33%), and two very high-boiling products (A) and (B), tentatively identified as amino-(amino-oxy)-substituted dimers of penta-1,4-diene (combined yield ca. 45%).

Products (A) and (B) were isolated together, contaminated with several minor unidentified products, and were identified by a consideration of the mass spectrum of the two-component mixture which showed peaks at m/e 288 (5%, $C_{12}H_{16}F_6N^+$), 287 (3%, $C_{12}H_{15}F_6N^+$), 247 (1%, $C_9H_{11}F_6N^+$), 246 (2%, $C_9H_{10}F_6N^+$), 166 (48%, $C_3H_2F_6N^+$), 136 (2%, $C_{10}H_{16}^+$), 135 (7%, $C_{10}H_{15}^+$), 121 (49%, $C_9H_{13}^+$), 79 (41%, $C_6H_7^+$), 69 (100%, CF_3^+), and 44 (96%, $CO_2^+/C_2H_4O^+$).

The i.r. spectrum of the adduct (122) showed absorptions at 3.24-3.42 (C-H str.), 6.09 (C:C str.), 7.25-8.57 (C-F str.), 9.54 (C-O-N str.), 10.08-10.75 (C-N str. and/or C-H def.), and 14.08 and 14.33 (CF_3 def.)μm.

The ^1H n.m.r. spectrum was poorly resolved and showed complex absorptions at δ ca. 2.10, 2.99, 3.87, 4.71 and 5.33 p.p.m., together with a broad singlet at δ 4.84 p.p.m., integrated intensities 2: 2: 1: 1: 1: 1, which were assigned to H_a, H_b, H_c, H_d, H_e, and H_f, respectively.



The ^{19}F n.m.r. spectrum showed absorptions at δ 28.95 (-8.3) (bs) and 19.3 (-18.0) (s) p.p.m., integrated intensities 1:1, assigned to fluorines in a sterically hindered $>CHON(CF_3)_2$ group, and a $-CH_2N(CF_3)_2$ group, respectively.

The mass spectrum showed peaks at m/e 346 [6%, $(M-C_3H_6)^+$],

220 {18%, $[\underline{M}-(CF_3)_2NO]^+$}, 179 (11%, $C_4H_3F_6N^+$), 166 [100%, $(CF_3)_2NCH_2^+$], and 68 (2%, $C_5H_8^+$).

The formation of the products may be explained by the mechanism outlined in Scheme 20.

Once again it is apparent that in contrast to the oxyl (6) reaction, the $(CF_3)_2N\cdot$ radical preferentially adds to the double bond rather than abstract an allylic hydrogen, to give the major product (122).

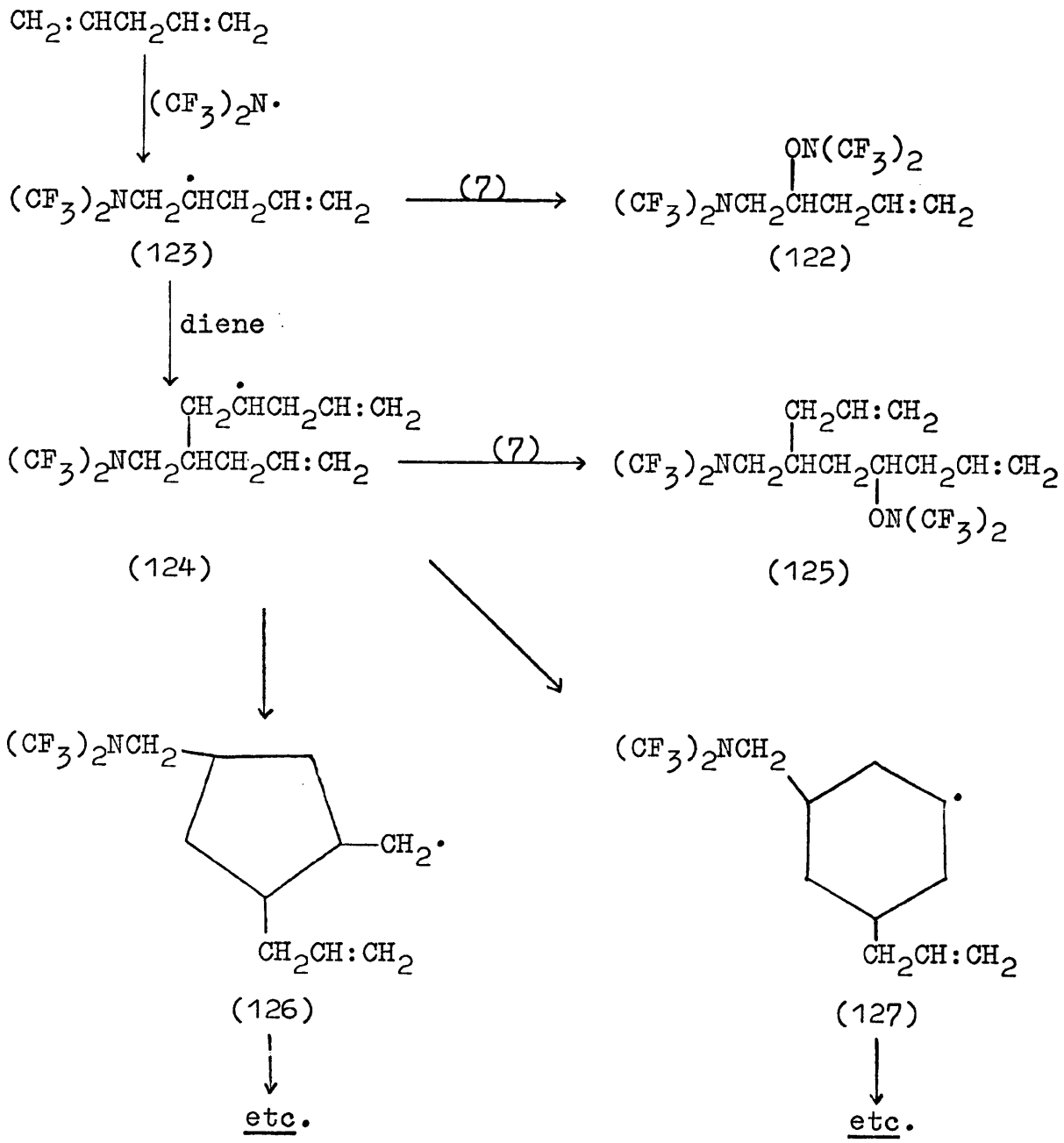
It was rather difficult to determine when the reactions had reached completion, although it was observed that the neat reaction mixture formed one layer on warming from -196 °C to room temperature. The fast rate of reaction may in part explain the complexity of the products, particularly in the neat reaction, as indicated by the lower yield of adduct (122) and the formation of the higher-boiling products (A) and (B).

Products (A) and (B) may arise <u>via</u> reaction of the intermediate (123) with the diene, to form intermediate (124) which may then be scavenged by the oxadiazapentane (7) to form compound (125), which may in turn be further scavenged by (7).

Alternatively, intermediate (124) may undergo cyclisation to form intermediates (126) and/or (127); the mass spectrum of the two-component mixture of products (A) and (B) was not sufficiently clear, however, to determine whether cyclisation had occurred. Although cyclisation of intermediate (123) would not be expected as it would involve an unfavourable four-membered transition state, intermediate (124) may cyclise <u>via</u> more favourable five-membered or six-membered.

A further explanation of the complexity of the reaction products may be that the intermediates (123), (124), (126), and (127) abstract an allylic hydrogen from the diene rather than undergo chain-transfer with the oxadiazapentane (7).

Reaction of the oxadiazapentane (7) with penta-1,4-diene



Scheme 20

Suggestions for future work

Compounds containing an allylic hydrogen have been shown to readily undergo hydrogen abstraction by the oxyl and it would be interesting to investigate whether benzene is formed in the reaction of the oxyl with cyclohexa-1,4-diene *via* abstraction of the two allylic hydrogen atoms.

The reaction of the oxadiazapentane with *t*-butylbenzene has indicated that with arylalkanes containing a relatively unreactive side-chain the $(CF_3)_2N\cdot$ radical preferentially attacks the aromatic ring, and a further extension of this work would be to investigate the extent of this type of reaction with other aromatic compounds using both the oxadiazapentane and the compounds $(CF_3)_2NX$ (where X= Cl, Br, I) as precursors to the $(CF_3)_2N\cdot$ radical.

The reaction between the oxadiazapentane and chlorobenzene was not fully characterised and further work is required both with this and other halogenobenzenes to identify the isomers obtained and investigate the extent of halogen rather than hydrogen atom substitution.

EXPERIMENTAL

General Techniques

Many of the compounds involved in this work were gases or volatile liquids of unknown toxicity, and were therefore manipulated in a conventional Pyrex glass vacuum system. The system comprised of a storage section with an attachment designed for the determination of molecular weights by Regnault's method, and a series of interconnected traps used for the separation of volatile compounds by fractional condensation *in vacuo*. Separate units of the trap section were connected by high-vacuum glass stopcocks and the pressure in each unit was accurately determined prior to use to facilitate the accurate measurement of the volumes of volatile materials handled. The whole system was evacuated by an Edward's Speedivac two-stage rotary oil pump to pressures of 10^{-2} to 10^{-3}mm Hg.

Reactions involving bistrifluoromethylamino-oxyl and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) were carried out under autogenous pressure in thick walled (3-4mm) Pyrex ampoules fitted with Rotaflo Teflon-sealed stopcocks. Non-volatile compounds were introduced into the ampoule before evacuating and were then carefully degassed. Volatile compounds were condensed into the ampoule at -196 °C *in vacuo* and the stopcock was then closed. The ampoule was allowed to warm slowly to room temperature before being further heated (if necessary).

Gas-phase reactions were carried out in Pyrex bulbs (*ca.* 10dm^3), by introducing the reactants into the evacuated bulb *via* an external trap (*ca.* 25cm^3) cooled to -196 °C.

The reactions involving bistrifluoromethylamino-oxyl (6) were considered to be complete when the purple colouration of the oxyl had disappeared. The completion of the reactions involving perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (7) were more difficult to determine, and it was found that when the reactions were worked up when only one layer was apparent rather than the original two, the reactions had only reached ca. 50% completion (e.g. 3,3,3-trichloropropene and cyclopropylphenylmethane); subsequent reactions were therefore left for twice the time that it had taken for one layer to become apparent.

On completion of the reaction, the ampoule was cooled to -196 °C, the stopcock opened, and the contents transferred in vacuo into the vacuum system.

Initial separation of reaction products was usually achieved by fractional condensation in vacuo. The gaseous mixture was passed, at a pressure of 1-2mm Hg, through a series of traps maintained at progressively lower temperatures by 'slush baths' which consisted of melting organic solvents contained in a Dewar vessel, details of which are listed below.

Solvent	Temperature (°C)
Melting ice	0
" carbon tetrachloride	-23
" chlorobenzene	-45
'Cardice'/methylated spirits	-78
Melting toluene	-95
" diethyl ether	-120

Solvent	Temperature (°C)
Melting petroleum ether	-140
Liquid nitrogen	-196

The purities of all starting materials were checked by infrared (i.r.) spectroscopy and gas liquid chromatography (g.l.c.) prior to use.

Pure compounds were isolated by fractional condensation in vacuo or by preparative-scale g.l.c. Preparative-scale g.l.c. work was conducted on a Pye 104 instrument using columns (2-6m) packed with acid-washed Celite coated with the following stationary phases (10-30% w/w); Apiezon L (APL), Kel F oils no. 10, Silicone elastomer (SE 30), Polyethyleneglycol adipate (PEGA), and Trixylyl phosphate (TXP).

Analytical g.l.c. work was carried out using a Pye 104 instrument fitted with columns (2-6m, 3-4mm i.d.) containing Celite coated with the above stationary phases, linked to a Hewlett-Packard 3352b Laboratory Data System Integrator for estimation of molar percentages of the reaction mixtures. Wherever possible the instrument was calibrated with mixtures of known composition.

Products were identified by elemental analysis, molecular weight determination [Regnault's method for gases and volatile liquids, and vapour-phase osmometry (Hitachi/Perkin-Elmer 115 instrument) for polymers], infrared(i.r.) spectroscopy [Perkin-Elmer 197 instrument using sodium chloride optics; gases in a gas cell (10cm path length) and liquids as a capillary film], nuclear magnetic resonance (n.m.r.) spectroscopy [Hitachi R20A instrument operating at

60.0 MHz for ^{1}H and 56.46 MHz and Varian Associates HA 100 instrument operating at 100.0 MHz for ^{1}H and 94.1 MHz for ^{19}F, with external T.M.S. and para-$Cl_2C_6H_4/CCl_4$ used as references for ^{1}H spectra, and with T.F.A., para-$CF_2ClSC_6H_4Cl$ and $CF_3SCH_2CHBrCH_2Br$ used as references for ^{19}F spectra], and mass spectrometry (linked AEI DS10 on-line computer and printout attached to an AEI MS 902 spectrometer).

Boiling points were determined by Siwoloboff's method.

The preparation of starting materials

1. Bistrifluoromethylamino-oxyl

A Pyrex ampoule (ca. 800cm^3) was charged with potassium permanganate (18.0g, 114mmol) and sulphuric acid (10%, 250cm^3), evacuated and kept at ca. -25 °C (12h).

NN-bistrifluoromethylhydroxylamine (25.0g, 147mmol) was then added in vacuo and the mixture allowed to warm to room temperature and then kept at this temperature (1d). The crude product was dried by passing the vapour over phosphoric oxide in vacuo and then purified by fractional condensation in vacuo to afford bistrifluoromethylamino-oxyl (6) (23.7g, 141 mmol, 96%), (which condensed as a yellow solid at -95 °C), and which was shown to be pure by i.r. spectroscopy.

2. Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)

Trifluoronitrosomethane (9.3g, 94mmol) and bistrifluoromethylamino-oxyl (20.6g, 123mmol) were sealed in vacuo in a Pyrex ampoule (ca. 800cm^3) and stored at room temperature (14d). The crude product was purified by fractional condensation in vacuo to afford a colourless liquid which condensed in traps cooled to -45 °C and -23 °C and was

identified[81] by i.r. and n.m.r. spectroscopy as perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (7) (24.7g, 77mmol, 82%).

3. 3,3,3-Trichloropropene

In a typical run, bromotrichloromethane (6.0g, 30.3mmol), ethylene (0.14g, 38mmol) and benzoyl peroxide (ca. 0.2g) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and maintained at 170-180 °C (4d). Several runs were carried out involving a total quantity of bromotrichloromethane (52g, 263mmol) and ethylene (0.9g, 320mmol). The products were removed from the ampoules, combined, and distilled to afford 1,1,1-trichloro-3-bromopropane (40g, 177mmol, 67% based on bromotrichloromethane), b.p. 76-78 °C at 22mm Hg (lit. b.p.[119] 97 °C at 50mm Hg).

Potassium hydroxide (20.1g) dissolved in methyl alcohol (50cm^3) was slowly added (45min) to the distillate with constant stirring, and the temperature of the stirred mixture maintained at ca. 25 °C with an ice-water bath (1h). The resulting material was poured into an ice-water mixture (100cm^3), and the organic layer separated, washed once with water (25cm^3), dried ($MgSO_4$) and fractionated to afford 3,3,3-trichloropropene (15.5g, 108mmol, 61%), b.p. 102-103 °C (lit. b.p.[120] 100-100.5 °C).

4. 3,3,3-Trichloro-2-methylpropene

1,1,1-Trichloro-2-methylpropanol (44.1g, 0.25mmol) was placed in a flask (1dm^3) fitted with a reflux condenser. Thionyl chloride (120g, 1.0mol) was added and the mixture warmed until evolution of hydrogen chloride ceased. Then

NN-dimethylaniline (1.7g) was slowly added and the mixture heated under reflux (7h). The volatile products were removed by condensation *in vacuo* and the remaining higher-boiling material fractionated to afford 3,3,3-trichloro-2-methylpropene (13.5g, 0.08mol, 30%), b.p. 132-137 °C (lit. b.p.[121] 130-137 °C), which was shown by n.m.r. spectroscopy and g.l.c. (2m SE 30 at 120 °C) to be contaminated with 1,1,3-trichloro-2-methylpropene (*ca.* 10%).

5. 2-Chloro-2-phenylpropane

Dry hydrogen chloride was slowly bubbled through α-methylstyrene (19.4g, 164mmol) maintained at *ca.* 0 °C by means of an ice-water bath (2h). The resulting liquid product was degassed and fractionated *in vacuo* to give 2-chloro-2-phenylpropane (21.5g, 139mmol, 85%), b.p. 62 °C at 2mm Hg (lit.b.p.[122] 82-83 °C at 11mm Hg), the purity of which was confirmed by i.r. and n.m.r. spectroscopy.

The reactions of bistrifluoromethylamino-oxyl (6)

1. With t-butyl bromide

The oxyl (6) (2.24g, 13.3mmol) and t-butyl bromide (0.98g, 7.2mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and stored at room temperature (30h). Analysis of the resulting mixture by g.l.c. (2m SE 30 and KEL F at 80 °C) showed that it contained seven major components (A-G) (both columns showed six major components with two different peaks overlapping in each case), and *ca.* four minor components which were not present in sufficient quantities to allow their separation and identification.

Components (A) and (B) were separated by fractional

condensation *in vacuo* and identified by i.r. spectroscopy and by a comparison of their g.l.c. retention times with those of known pure samples as NN-bistrifluoromethylhydroxylamine (*ca.* 0.93g, *ca.* 5.5mmol, *ca.* 41% based on oxyl) and unchanged *t*-butyl bromide (0.25g, 1.8mmol, 25% recovered).

Components (C-G) were separated by preparative-scale g.l.c. (2m SE 30 at 90 °C) to give (i) 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methylpropane (C) $(CF_3)_2NOCH_2CMe_2ON(CF_3)_2$ (0.21g, 0.5mmol, 10%), which was identified by comparing its i.r., n.m.r., and mass spectra with those reported previously,[82] (ii) 1,2,3-tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane (D) $[(CF_3)_2NOCH_2]_2CMeON(CF_3)_2$ (0.30g, 0.5mmol, 10%) (Found: C, 21.6; H, 1.1; N, 7.6; F, 61.7. $C_{10}H_7F_{18}N_3O_3$ requires C, 21.5; H, 1.3; N, 7.5; F, 61.2%), b.p. 163 °C, which was identified by a consideration of its i.r. (p.226), n.m.r. (p. 240), and mass (p. 260) spectra, (iii) 1-(NN-bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane (E) $(CF_3)_2NOCH_2CMe_2Br$ (0.55g, 1.8mmol, 33.5%) (Found: C, 23.6; H, 2.7; Br, 25.8; N, 4.9; F, 37.6. $C_6H_8BrF_6NO$ requires C, 23.7; H, 2.6; Br, 26.3; N, 4.6; F, 37.5%), b.p. 132 °C, which was identified by a consideration of its i.r. (p.226), n.m.r. (p. 240), and mass (p. 260) spectra, (iv) 1,2-bis(NN-bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane (F) $(CF_3)_2NOCH_2CMe(CH_2Br)ON(CF_3)_2$ (0.39g, 0.8mmol, 15.5%) (Found: C, 20.7; H, 1.5; N, 6.0. $C_8H_7BrF_{12}N_2O_2$ requires C, 20.4; H, 1.5; N, 5.9%), b.p. 170 °C, which was identified by a consideration of its i.r. (p.226), n.m.r. (p. 240), and mass

(p. 261) spectra (the mass spectrum was identical to that previously reported[95]), and (v) 1,2-dibromo-2-methylpropane (G) (0.31g, 1.4mmol, 26.5%) (Found: C, 22.0; H, 4.0; Br, 73.7. Calc. for $C_4H_8Br_2$: C, 22.2; H, 3.7; Br, 74.1%), which was identified by a comparison of its i.r., n.m.r., and mass spectra with those of a known pure sample.

2. With t-butyl chloride

The oxyl (6) (1.57g, 9.3mmol) and t-butyl chloride (0.43g, 4.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 50cm^3) and stored at room temperature (13d). The products were separated by fractional condensation in vacuo into the following two fractions.(a) A fraction which condensed below -78 °C (0.10g; M, 43), which was shown by i.r. spectroscopy to consist of hydrogen chloride (ca. 0.07g, ca. 2.0mmol, ca. 61%) and an unidentified fluorinated compound which showed absorptions in the region 7.70-8.22 (C-F str.)μm. (b) A dark yellow liquid (1.90g), which was shown by g.l.c. (2m SE 30 and KEL F at 65 °C) to contain thirteen components (A-M). By a comparison of the retention times of components (A) and (B) with those of known pure samples, they were identified as NN-bistrifluoromethylhydroxylamine (ca. 0.20g, ca. 1.2mmol, ca. 13% based on oxyl) and unchanged t-butyl chloride (ca. 0.13g, ca. 1.4mmol, ca. 30% recovered)

Components (F), (K), and (L) were separated by preparative-scale g.l.c. (2m SE 30 at 75 °C) to give (i) 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methylpropane (F) (ca. 0.46g, ca. 1.2mmol, ca. 37%), and (ii) 1,2,3-tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane (K) (ca. 0.14g,

ca. 0.3mmol, ca. 8%), which were identified by a comparison of their i.r., n.m.r., and mass spectra with those of previously obtained pure samples (p. 178), and (iii) 1,2-bis(NN-bistrifluoromethylamino-oxy)-3-chloro-2-methylpropane (L) $(CF_3)_2NOCH_2CMe(CH_2Cl)ON(CF_3)_2$ (ca. 0.04g, ca. 0.1mmol, ca. 3.5%), which was identified by a consideration of its i.r. (p. 227), n.m.r. (p. 241), and mass (p. 261) spectra; (the mass spectrum was virtually identical to that reported previously[95]).

3a. With 2,2-dichloropropane at 70-80 °C

The oxyl (6) (2.34g, 13.9mmol) and 2,2-dichloropropane (0.78g, 6.9mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and maintained at 70-80 °C (78d). The products were separated by consensation in vacuo into the following two fractions. (a) A fraction which condensed below -78 °C (ca. 0.42g, ca. 4.6mmol; M, 92), which was shown by i.r. spectroscopy to contain hydrogen chloride, NN-bistrifluoromethylamine, and carbon dioxide and which was not investigated further. (b) A light-yellow liquid (ca. 2.70g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylhydroxylamine; several absorptions were also present in the region 5.45-5.85 (C:O str.)μm . The fraction was shown by g.l.c. (2m SE 30 and KEL F at 80 °C) to contain unchanged 2,2-dichloropropane (ca. 0.40g, ca. 3.5mmol, ca. 50% recovered) and NN-bistrifluoromethylhydroxylamine (ca. 0.76g, ca. 4.5mmol, ca. 32% based on oxyl), which were identified by a comparison of their g.l.c. retention times with those of known pure samples, together with seven components (A-G) in

the ratio 1.4: 4.6: 16.2: 9.4: 2.5: 1.0: 5.1.

Component (D) was separated by preparative-scale g.l.c. (4m KEL F at 80 °C) and was identified as 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-chloropropane $(CF_3)_2NOCH_2CMeClON(CF_3)_2$ (ca. 0.33g, ca. 0.8mmol, ca. 24%) (Found: C, 20.6: H, 1.1; N, 6.8. $C_7H_5ClF_{12}N_2O_2$ requires C, 20.4; H, 1.2; N, 6.8%), b.p. 135 °C, by a consideration of its i.r. (p. 227), n.m.r. (p. 241), and mass (p. 262) spectra.

Component (C) was partially separated by preparative-scale g.l.c. (as above) contaminated with unchanged 2,2-dichloropropane and was tentatively identified as 1-(NN-bistrifluoromethylamino-oxy)-2,2-dichloropropane $(CF_3)_2NOCH_2CMeCl_2$ (ca. 0.42g, ca. 1.5mmol., ca. 42%) by a consideration of the n.m.r. (p. 241) and mass (p. 262) spectra of the two-component mixture.

3b. With 2,2-dichloropropane at room temperature

The oxyl (6) (4.48g, 26.7mmol) and 2,2-dichloropropane (1.44g, 12.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and stored at room temperature (440d). Condensation of the products in vacuo gave the following fractions. (a) A volatile fraction (2.94g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, and hydrogen chloride; the spectrum also showed absorptions in the region 3.33-3.45 (C-H str.)μm, probably indicative of unreacted dichloropropane. The fraction was not investigated further. (b) A colourless non-volatile liquid (2.98g), which was shown by g.l.c. (2m SE 30 and KEL F at 80 °C) to contain NN-bistri-

fluoromethylhydroxylamine (trace), unchanged dichloropropane (yield not determined), and components (C), (D), (F), and (G) in the ratio 5.2: 5.5: 1.0: 1.4. Components (A), (B), and (E) were not detected in the reaction products, and the i.r. spectrum of the mixture showed strong absorptions in the region 5.38-5.95 (C:O str.)μm.

4. With 1,1,1-trichloroethane

The oxyl (6) (3.34g, 19.9mmol) and 1,1,1-trichloroethane (1.37g, 10.3mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 300cm^3) and stored at room temperature (620d). As the reaction had not reached completion in this period, as shown by the presence of oxyl colour, the reaction tube was transferred to an oven and kept at 70-80 °C (240d). Work up of the products showed that a quantity of material (0.58g) had been lost, probably due to leakage at the Rotaflow tap whilst in the oven, Fractional condensation of the products *in vacuo* gave (a) a purple gas which condensed at -196 °C (1.94g; M, 132), which was shown by i.r. spectroscopy to contain unreacted oxyl (6), NN-bistrifluoromethylamine and carbon dioxide, and which was not investigated further, and (b) a colourless liquid which condensed at -78 °C (2.12g) and was shown by g.l.c. (2m PEGA at 85 °C) to contain two major components and four very minor components which were not present in sufficient quantities to allow their separation and identification. By comparison of the retention time of the two main components with those of known pure samples, they were identified as unchanged trichloroethane (*ca.* 1.3g, *ca.* 9.8mmol, *ca.* 95% recovered), and NN-bistrifluoromethyl-

hydroxylamine (ca. 0.42g, ca. 2.5mmol, ca. 12.5% based on oxyl).

A white solid (ca. 0.07g), which remained in the tube was not investigated further.

5. With 2-chloro-2-phenylpropane

The oxyl (6) (1.88g, 11.2mmol) and 2-chloro-2-phenylpropane (0.87g, 5.6mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and kept at room temperature (35min). Fractional condensation of the products in vacuo gave (a) a -196 °C fraction (0.17g; M, 38), which was shown by i.r. spectroscopy to consist mainly of hydrogen chloride (ca. 0.14g, 3.7mmol, 97.5%), together with NN-bistrifluoromethylamine (trace) and NN-bistrifluoromethylhydroxylamine (trace), (b) a -78 °C fraction (0.24g), which was shown by i.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (ca. 0.23g, ca. 1.4 mmol, ca. 12.5% based on oxyl) contaminated with a trace amount of NN-bistrifluoromethylamine, and (c) a colourless non-volatile liquid (2.32g), which was shown by g.l.c. (2m APL and PEGA at 150 °C) to contain two major components (A) and (B) and ca. eight minor components which were not present in sufficient quantities to allow their separation and identification. By a comparison of the retention time of component (B) with that of a known pure sample it was identified as unchanged 2-chloro-2-phenylpropane (0.28g, 1.8mmol, 32.5% recovered) (which decomposes to α-methylstyrene at 150 °C on the g.l.c. column).

Component (A) was separated by preparative-scale g.l.c. (4m APL at 140 °C) to afford 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-phenylpropane $(CF_3)_2NOCH_2CPhMeON(CF_3)_2$ (1.34g,

3.0mmol, 78% based on consumed chloride) (Found: C, 34.4; H, 2.3; N, 6.5; F, 50.6. $C_{13}H_{10}F_{12}N_2O_2$ requires C, 34.4; H, 2.2; N, 6.2; F, 50.2%), which was identified by a consideration of its i.r. (p. 227), n.m.r. (p. 242), and mass (p. 263) spectra. (d) A white solid (ca. 0.02g), which remained in the tube was not investigated further

6a. With 3,3,3-trichloropropene at room temperature

The oxyl (6) (4.67g, 27.7mmol) and 3,3,3-trichloropropene (2.10g, 14.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and stored at room temperature (6d). Condensation of the products in vacuo gave (a) a volatile fraction (0.14g), which was shown by i.r. spectroscopy to consist of unchanged 3,3,3-trichloropropene, NN-bistrifluoromethylamine, and NN-bistrifluoromethylhydroxylamine and was not investigated further, and (b) a colourless non-volatile liquid (6.64g), which was shown by g.l.c. (2m TXP and SE 30 at 130 °C) to contain two components (A and B) in the ratio 44.2: 1. By a comparison of the retention time of the minor component (B) with that of a known pure sample it was identified as 1,3-bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane (0.15g, 0.3mmol, 2.5%) (see p. 185).

The major component (A) was separated by preparative-scale g.l.c. (2m SE 30 at 120 °C) to afford 1,2-bis(NN-bistrifluoromethylamino-oxy)-3,3,3-trichloropropane $(CF_3)_2NOCH_2CH(CCl_3)ON(CF_3)_2$ (6.4g, 13.3mmol, 97%) (Found: C, 17.7; H, 0.5; Cl, 22.4; N, 6.0; F, 47.9. $C_7H_3Cl_3F_{12}N_2O_2$ requires C, 17.5; H, 0.6; Cl, 21.9; N, 5.8; F, 47.5%), b.p. 171 °C, which was identified by a consideration of its

i.r. (p. 228), n.m.r. (p. 242), and mass (p. 264) spectra.

6b. With 3,3,3-trichloropropene in the gas phase

The oxyl (6) (3.32g, 19.7mmol) and 3,3,3-trichloropropene (1.34g, 9.2mmol) were sealed in vacuo in a Pyrex bulb (ca. 10dm^3) and maintained at 70-80 °C (6d). Condensation of the products in vacuo gave (a) a volatile fraction (0.24g), which was shown by i.r. spectroscopy to contain unchanged oxyl (6) and NN-bistrifluoromethylhydroxylamine, and was not investigated further, and (b) a colourless non-volatile liquid (4.41g), which was shown by g.l.c. (2m TXP and SE 30 at 130 °C) to contain two major components (A and B) in the ratio 1: 5.2, and four minor components which were not present in sufficient quantities to allow their separation and identification. By a comparison of the retention time of component (A) with that of a pure sample obtained previously (p. 184), it was identified as 1,2-bis(NN-bistrifluoromethylamino-oxy)-3,3,3-trichloropropane (0.63g, 1.3mmol, 15%).

Component (B) was separated by preparative-scale g.l.c. (2m SE 30 at 120 °C) to afford 1,3-bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane $(CF_3)_2NOCH_2CHClCCl_2ON(CF_3)_2$ (3.39g, 7.0mmol, 77%) (Found: C, 17.8; H, 0.6; Cl, 21.9; N, 6.0. $C_7H_3Cl_3F_{12}N_2O_2$ requires C, 17.5; H, 0.6; Cl, 21.9; N, 5.8%), which was identified by a consideration of its i.r. (p. 228), n.m.r. (p. 242), and mass (p. 265) spectra.

7. With 3,3,3-trichloro-2-methylpropene

The 3,3,3-trichloro-2-methylpropene (p. 176) used in the following reaction was only 90% pure, the contaminant being 1,1,3-trichloro-2-methylpropene.

The oxyl (6) (3.23g, 19.2mmol) and the trichloropropene (1.55g, 9.7mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and stored at room temperature (1h). The products were separated by fractional condensation *in vacuo* into a volatile fraction (0.23g; *M*, 125) and a non-volatile colourless liquid (4.56g).

The volatile fraction on further fractional condensation *in vacuo* gave (a) a -196 °C fraction (*ca.* 0.04g), which was shown by i.r. spectroscopy to consist of unchanged oxyl (*ca.* 0.02g, *ca.* 0.1mmol, *ca.* 0.5% recovered) and hydrogen chloride (*ca.* 0.02g, *ca.* 0.6mmol, *ca.* 6%), and (b) a -78 °C fraction (0.17g), which was shown by i.r. spectroscopy to be *NN*-bistrifluoromethylhydroxylamine (0.17g, 1.0mmol, 5% based on oxyl).

The non-volatile liquid was shown by g.l.c. (2m TXP at 120 °C) to contain four components (A-D) in the ratio 1: 36.4: 4: 1. Component (B) was separated by preparative-scale g.l.c. (as above) and estimated and identified by n.m.r. spectroscopy (p. 243) and mass spectrometry (p. 266) as a mixture of the two isomers (ratio *ca.* 2:1) 1,2-bis(*NN*-bistrifluoromethylamino-oxy)-2-methyl-3,3,3-trichloropropane $(CF_3)_2NOCH_2CMe(CCl_3)ON(CF_3)_2$ and 1,3-bis(*NN*-bistrifluoromethylamino-oxy)-2-methyl-2,3,3-trichloropropane $(CF_3)_2NOCH_2CMeClCCl_2ON(CF_3)_2$ (combined yield: 4.03g, 8.1mmol, 84%) (Found: C, 19.7; H, 1.1; Cl, 21.5; N, 6.0%. Calc. for $C_8H_5Cl_3F_{12}N_2O_2$: C, 19.4; H, 1.0; Cl, 21.5; N, 5.7%). The i.r. spectrum of component (B) showed absorptions typical of an amino-oxy group at 7.5-8.3 (C-F str.), 10.6 (C-N str.), and 14.08 (CF_3 def.)μm, together with bands at 11.98 and 12.4

(C-Cl str.)μm

On the basis of coupled g.l.c. (as above)/mass spectrometry (p. 267) component (C) was tentatively identified as 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methyl-1,1,3-trichloropropane $(CF_3)_2NOCCl_2CMe(CH_2Cl)ON(CF_3)_2$ (0.45g, 0.9mmol, 9%); its n.m.r. spectrum (p. 243) (as a mixture with several other components) was consistent with the proposed structure. The coupled g.l.c./mass spectra of the minor components indicated that component (D) was an amino-oxy adduct (m/e 69, 100%), but component (A) could not be identified.

8. With t-butylbenzene

The oxyl (6) (2.43g, 14.5mmol) and t-butylbenzene (0.61g, 4.5mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (3d). Condensation of the products in vacuo gave (a) a volatile fraction (1.07g), which was shown by i.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (1.07g, 6.3mmol, 43% based on oxyl), and (b) a light yellow non-volatile (1.97g), which was shown by g.l.c. (2m TXP and APL at 140 °C) to contain two major components (A and B) and ca. sixteen minor components.

The two main components were separated by preparative-scale g.l.c. (2m TXP at 140 °C) to afford unchanged t-butylbenzene (B) (0.13g, 0.9mmol, 21% recovered) and 1-(NN-bistrifluoromethylamino-oxy)-2-methyl-2-phenylpropane (A) $(CF_3)_2NOCH_2CMe_2Ph$ (0.30g, 1.0mmol, 28%) (Found: C, 47.7; H, 4.2; N, 4.8; F, 37.9. $C_{12}H_{13}F_6NO$ requires C, 47.8; H, 4.3; N, 4.7; F, 37.9%), which was identified by a consideration of its i.r. (p. 229), n.m.r. (p. 245), and mass (p. 270) spectra.

Two minor components were also separated, and although not completely pure, were tentatively identified as a NN-bistrifluoromethylamino-t-butylbenzene $(CF_3)_2NC_6H_4CMe_3$ (ca. 0.08g, ca. 0.3mmol, ca. 8%) and 4-NN-bistrifluoromethylamino-t-butylbenzene p-$(CF_3)_2NC_6H_4CMe_3$ (ca. 0.06g, ca. 0.23 mmol, ca. 6%) by a comparison of their n.m.r. spectra and g.l.c. retention times with those of previously obtained pure samples (p. 211).

The i.r. spectrum of the high-boiling mixture showed absorptions in the region 5.78-5.99 (C:O str.)μm, and thus it is considered that multi-substitution at one carbon centre, resulting in ester-type products, had occurred to some extent.

9. With 2,2-diphenylpropane

The reaction of a 2:1 molar mixture of the oxyl (6) and 2,2-diphenylpropane at room temperature (8d) gave unchanged alkane (56% recovered) and a complex mixture of high-boiling products. Hence, the reaction was repeated using a larger molar ratio of oxyl:alkane as outlined below.

The oxyl (6) (2.45g, 14.6mmol) and 2,2 diphenylpropane (0.65g, 3.3mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and maintained at 70-80 °C (3d). Condensation of the products in vacuo gave (a) a volatile fraction (1.14g), which was shown by i.r. and n.m.r. spectroscopy to consist almost entirely of NN-bistrifluoromethylhydroxylamine (ca. 1.12g, 6.6mmol, 45% based on oxyl), contaminated with NN-bistrifluoromethylamine (trace), and (b) a brown non-volatile liquid (1.96g), which was shown by g.l.c. (2m SE 30 and APL at 190 °C) to contain ca. fifteen components.

One component was separated by preparative-scale g.l.c. (2m APL at 180 °C) and identified as unchanged 2,2-diphenylpropane (ca. 0.07g, ca. 0.4mmol, ca. 11% recovered). Another component was partially separated by preparative-scale g.l.c. (as above) contaminated with an unidentified amino-oxy-substituted product, and was tentatively identified as 1-(NN-bistrifluoromethylamino-oxy)-2,2-diphenylpropane $(CF_3)_2NOCH_2CMePh_2$ (ca. 0.37g, ca. 1.0mmol, ca. 36%), on the basis of the n.m.r. spectra (p. 246) of the two-component mixture. Separation of the other components was not possible due to their intractibility and decomposition under the g.l.c. conditions.

The i.r. spectrum of the non-volatile mixture showed absorptions in the region 5.65-5.92 (C:O str.)μm, indicating that multi-substitution at one carbon centre, resulting in ester-type products, had occurred to some extent.

10. With 2-phenylpropan-2-ol

The oxyl (6) (2.55g, 15.2mmol) and 2-phenylpropan-2-ol (1.05g, 7.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (3d). Condensation of the products in vacuo gave (a) a volatile fraction (0.56g; M, 104), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, and carbon dioxide and which was not investigated further, and (b) a light brown non-volatile liquid (ca. 2.9g), which showed absorptions in its i.r. spectrum in the regions 2.78-3.13 (O-H str.), 5.71-5.95 (C:O str.), and 6.25 (C:C str.)μm, and which was shown by g.l.c. (2m PEGA

and SE 30 at 190 °C) to contain one major component (A), ca. eleven minor low-boiling components, and three very high-boiling components (B-D), in the ratio (A-D) 34.7: 1.0: 11.5: 8.0. By a comparison of the retention times of components (B-D) with the three high-boiling components obtained in the reaction of 2-phenylpropan-2-ol with NN-bistrifluoromethylhydroxylamine (p. 224), they were tentatively identified as isomeric dimers of α-methylstyrene (combined yield ca. 30%).

The major product (A) was separated by preparative-scale g.l.c. (2m PEGA at 130 °C) to afford 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-phenylpropane (ca. 1.75g, 3.9mmol, 50%), which was identified by a comparison of its i.r., n.m.r., and mass spectra with those of a previously obtained pure sample (p. 183), and (c) a dark brown solid (ca. 0.15g), which remained in the tube was not investigated further.

11. With t-butyl acetate

The oxyl (6) (2.43g, 14.5mmol) and t-butyl acetate (0.79g, 6.8mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (41d). The products were separated by condensation in vacuo to afford the following. (a) A fraction which condensed below -78 °C (0.06g) and was shown by i.r. spectroscopy to be NN-bistrifluoromethylamine (ca. 0.06g, ca. 0.4mmol, ca. 3% based on oxyl). (b) A colourless liquid (3.16g), which was shown by g.l.c. (2m SE 30 at 90 °C) to contain four major components and ca. twelve minor components which were not present is sufficient quantities to allow their separation and identification.

The four major components were separated by preparative-

scale g.l.c. (as above) to afford (i) NN-bistrifluoromethylhydroxylamine (1.20g, 7.1mmol, 49% based on oxyl), (ii) unchanged t-butyl acetate (0.40g, 3.5mmol, 51% recovered), (iii) 1,1-dimethyl-2-(NN-bistrifluoromethylamino-oxy)-2-oxoethyl acetate $(CF_3)_2NOCOCMe_2OAc$ (0.39g, 1.3mmol, 40%) (Found: C, 32.1; H, 3.2; N, 4.4. $C_8H_9F_6NO_4$ requires C, 32.3; H, 3.0; N, 4.7%), b.p. 163 °C, which was identified by a consideration of its i.r. (p. 231), n.m.r. (p. 246), and mass (p. 274) spectra, and (iv) a product which was shown by g.l.c. (2m TXP at 90 °C) to be a mixture of two components in the ratio ca. 2.8: 1. These components were tentatively identified on the basis of n.m.r. spectroscopy (p. 247) and mass spectrometry (p. 275) as 1,1-dimethyl-2-(NN-bistrifluoromethylamino-oxy)ethyl acetate $(CF_3)_2NOCH_2CMe_2OAc$ (ca. 0.34g, ca. 1.2mmol, ca. 36%) and 1,1-dimethyl-2,2-bis(NN-bistrifluoromethylamino-oxy)ethyl acetate $\left[(CF_3)_2NO\right]_2CHCMe_2OAc$ (ca. 0.23g, ca. 0.5 mmol, ca. 15%). The i.r. spectrum of the two-component mixture showed very strong absorptions in the region 7.41-8.47 (C-F str.)μm together with a strong broad absorption at 5.77 (C:O str.)μm.

12. Cyclopropylcarbinol

The reaction of a 2:1 molar mixture of the oxyl(6) and cyclopropylcarbinol at room temperature (10min) gave NN-bistrifluoromethylhydroxylamine, unchanged alcohol (56% recovered), and one major component (A) (ca. 95% based on consumed alcohol). Hence, the reaction was repeated using a larger molar ratio of oxyl:alcohol as follows.

The oxyl (6) (2.9g, 17.3mmol) and cyclopropylcarbinol

(0.32g, 4.4mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and kept at room temperature (10min). Fractional condensation of the products *in vacuo* gave (a) a -78 °C fraction (1.98g), which was shown by i.r. spectroscopy to be *NN*-bistrifluoromethylhydroxylamine (1.98g, 11.7mmol, 68% based on oxyl), (b) a -23 °C fraction (0.26g), which was shown by g.l.c. (2m SE 30 and PEGA at 80 °C) to contain two components, and (c) a colourless non-volatile liquid (0.98g), which was shown by g.l.c. (as above) to contain three components, two of which were identical to those present in fraction (b).

Fractions (b) and (c) were combined and the minor component was identified by a comparison of its g.l.c. retention time with that of a known pure sample as unchanged cyclopropylcarbinol (*ca.* 0.07g, *ca.* 0.1mmol, *ca.* 2.5% recovered).

The two major components (A) and (B) were separated by preparative-scale g.l.c. (as above) to afford *NN*-bistrifluoromethylhydroxylamine (B) (0.2g, 1.2mmol, 7% based on oxyl), and *NN*-bistrifluoromethylamino-oxycyclopropane carboxylate (A) $\overline{CH_2CH_2}CHCOON(CF_3)_2$ (1.04g, 4.4mmol, 99%) (Found: C, 30.2; H, 2.2; N, 5.9; F, 48.5. $C_6H_5F_6NO_2$ requires C, 30.4; H, 2.1; N, 5.9; F, 48.1%), which was identified by a consideration of its i.r. (p. 231), n.m.r. (p. 247), and mass (p. 274) spectra.

13. *With cyclopropylmethylcarbinol*

The oxyl (6) (3.95g, 23.6mmol) and cyclopropylmethylcarbinol (0.95g, 11.0mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and kept at room temperature (2min).

Fractional condensation of the products *in vacuo* gave (a) a -196 °C fraction (*ca.* 0.05g), which was shown by i.r. spectroscopy to be NN-bistrifluoromethylamine (*ca.* 0.05g, *ca.* 0.3mmol, *ca.* 1.5% based on oxyl), (b) a -78 °C fraction (1.94g), which was shown by i.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (1.94g, 11.5mmol, 49% based on oxyl), (c) a -23 °C fraction (1.3g), which was shown by g.l.c. (2m PEGA at 80 °C) to be a mixture of *ca.* seven components, and (d) a colourless non-volatile liquid (1.61g), which was shown by g.l.c. (as above) to be a complex mixture of *ca.* eleven components including those present in fraction (c).

Fractions (c) and (d) were combined and shown by g.l.c. (as above) to contain one major component and *ca.* ten minor components.

The major component was separated by preparative-scale g.l.c. (as above) to afford cyclopropylmethylketone $\overline{CH_2CH_2}CHCOCH_3$ (*ca.* 0.53g, *ca.* 6.3mmol, *ca.* 60%), which was identified by a comparison of its i.r. and n.m.r. spectra with those of a known pure sample. The i.r. spectrum of a mixture of the minor components showed absorptions in the region 6.0-6.77 (C:C str.)μm, together with O-H and C:O absorptions, and bands typical of an amino-oxy group.

14a. *With cyclopropylphenylmethane (neat)*

The oxyl (6) (3.16g, 18.8mmol) and cyclopropylphenylmethane (1.25g, 9.5mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and kept at room temperature (10min). Condensation of the products *in vacuo* gave (a) a -78 °C

fraction (1.6g), which was shown by i.r. and n.m.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (1.6g, 9.2 mmol, 49% based on oxyl), and (b) a colourless non-volatile liquid (2.81g), which was shown by g.l.c. (2m APL at 150 °C) to contain two major components (A) and (B) in the ratio 10.1: 1, and six very minor components which were not present in sufficient quantities to allow their separation and identification.

By a comparison of its retention time with that of a known pure sample, component (B) was identified as unchanged cyclopropylphenylmethane (0.1g, 0.8mmol, 9% recovered). Component (A) was separated by preparative-scale g.l.c. (as above) to afford cyclopropyl-(NN-bistrifluoromethylamino-oxy)phenylmethane $\overline{CH_2CH_2}CHCHPhON(CF_3)_2$ (2.47g, 8.3mmol, 95%), (Found: C, 48.3; H, 3.8; N, 4.9; F, 38.3. $C_{12}H_{11}F_6NO$ requires: C, 48.2; H, 3.7; N, 4.7; F, 38.1%), b.p. 201-202 °C, which was identified by a consideration of its i.r. (p. 232), n.m.r. (p. 248), and mass (p. 276) spectra.

14b. With cyclopropylphenylmethane (in solution)

The oxyl (6) (1.98g, 11.8mmol), cyclopropylphenylmethane (2.68g, 20.3mmol), and 1,1,2-trichloro-1,2,2-trifluoroethane (37.7g) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and kept at room temperature (10min). Condensation of the products in vacuo gave (a) a volatile fraction (38.66g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylhydroxylamine and 1,1,2-trichloro-1,2,2-trifluoroethane and which was not investigated further, and (b) a light yellow non-volatile fraction (3.71g), which was shown by

g.l.c. (2m APL at 150 °C) to contain three major components (A-C) in the ratio 1: 10.7: 31.9, and six very minor components. By a comparison of the retention times of components (C) and (B) with those of known pure samples they were identified as unchanged cyclopropylphenylmethane (C) (1.92g, 14.5mmol, 71.5% recovered) and cyclopropyl(NN-bis-trifluoromethylamino-oxy)phenylmethane (B) (1.47g, 4.9mmol, 84.5%). Component (A) was not identified.

15a. With 2(10)-pinene (β-pinene) (neat reactants)

The oxyl (6) (1.79g, 10.7mmol) and 2(10)-pinene (0.77g, 5.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3). The reaction reached completion as the mixture warmed up from -196 °C to room temperature. Consensation of the products in vacuo gave (a) a volatile fraction (0.46g), which was shown by i.r. spectroscopy to be NN-bistrifluoromethyl-hydroxylamine (0.46g, 2.7mmol, 26% based on oxyl), and (b) a colourless non-volatile liquid (2.1g), which was shown by g.l.c. (2m SE 30 at 130 °C) to contain unchanged 2(10)-pinene (0.15g, 1.1mmol, 19% recovered), identified by a comparison of its retention time with that of a known pure sample, and four major components (A-D) in the ratio 5.4: 1.0: 1.7: 2.9.

Components (A-D) were separated by preparative-scale g.l.c. (as above) to afford (i) 10-(NN-bistrifluoromethyl-amino-oxy)-2-pinene $(CF_3)_2NOCH_2C{:}CHCH_2CHCH_2CHCMe_2$ (A) (0.67g, 2.2mmol, 48%) (Found: C, 47.7; H, 5.1; N, 4.7; F, 38.0. $C_{12}H_{15}F_6NO$ requires C, 47.5; H, 5.0; N, 4.6; F, 37.6%), b.p. 184 °C, which was identified by a consideration of its i.r. (p. 232), n.m.r. (p. 248), and mass (p. 277) spectra, (iii)

1-(NN-bistrifluoromethylamino-oxy)methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene $(CF_3)_2NOCH_2C{:}CHCH_2CH[CMe_2ON(CF_3)_2]CH_2CH_2$ (B) (0.22g, 0.47mmol, 10%) (Found: C, 34.4; H, 3.2; N, 6.1; F, 49.1. $C_{14}H_{16}F_{12}N_2O_2$ requires C, 35.6; H, 3.4; N, 5.9; F, 48.3%), which was identified by a consideration of its i.r. (p. 232), n.m.r. (p. 249), and mass spectra (p. 278), and (iii) components (C) (0.36g, 0.8mmol, 16.5%) (Found: C, 35.5; H, 3.5; N, 6.2; F, 48.7%), b.p. 218 °C, and (D) (0.52g, 1.1mmol, 24%) (Found: C, 35.3; H, 3.7; N, 5.6; F, 48.5%), b.p. 220 °C, which were identified as diastereoisomers of 2(10)-bis(NN-bistrifluoromethylamino-oxy)pinane $(CF_3)_2NOCH_2CON(CF_3)_2CH_2CH_2CHCH_2CHCMe_2$, by a consideration of their i.r. (p. 233), n.m.r. (p. 250), and mass (p. 279) spectra.

15b. With 2(10)-pinene (in solution)

The oxyl (6) (3.38g, 20.1mmol) was slowly passed through a solution of 2(10)-pinene (1.36g, 10.0mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (38g) using nitrogen as carrier gas (30min). The lower-boiling material was removed by condensation in vacuo, and the remaining colourless non-volatile liquid (3.5g) was shown by g.l.c. (2m SE 30 at 130 °C) to contain unchanged 2(10)-pinene (11.5% recovered), and components (A-D) from the previous experiment in the ratio (A) (64%), (B) (7%), (C) (11%), and (D) (18%).

16. With 2-pinene (α-pinene)

The oxyl (6) (1.73g, 10.3mmol) and 2-pinene (0.76g, 5.6 mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3). The reaction reached completion as the mixture warmed from

-196 °C to room temperature. Condensation of the products *in vacuo* gave (a) a volatile fraction (*ca.* 0.65g), which was shown by i.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (0.65g, 3.8mmol, 37% based on oxyl), and (b) a light brown non-volatile liquid (1.84g), which was shown by g.l.c. (2m SE 30 at 145 °C) to contain unchanged 2-pinene (*ca.* 0.03g, *ca.* 0.3mmol, *ca.* 4.5% recovered), and two major components (A) and (B), and four minor components which were not present in sufficient quantities to allow their separation and identification.

Components (A) and (B) were separated by preparative-scale g.l.c. (4m SE 30 followed by 2m TXP at 140 °C) to afford (i) 3-(NN-bistrifluoromethylamino-oxy)-2(10)-pinene $CH_2{:}\overset{\frown}{C}CHON(CF_3)_2CH_2\underset{\frown}{CHCH_2}\overset{\frown}{CHCMe_2}$ (A) (1.09g, 3.6mmol, 66.5%) (Found: C, 47.8; H, 5.1; N, 4.9; F, 37.9. $C_{12}H_{15}F_6NO$ requires: C, 47.5; H, 5.0; N, 4.6; F, 37.6%), which was identified by a consideration of its i.r. (p. 233), n.m.r. p. 249), and mass (p. 280) spectra, and estimated by n.m.r. spectroscopy to be an equimolar mixture of exo- and endo-diastereoisomers, and (ii) 2,3-bis(NN-bistrifluoromethylamino-oxy)pinane $(CF_3)_2NO\overset{\frown}{C}MeCH\left[ON(CF_3)_2\right]CH_2\underset{\frown}{CHCH_2}\overset{\frown}{CHCMe_2}$ (B) (0.52g, 1.1mmol, 20.5%) (Found: C, 35.9; H, 3.5; N, 5.8; F, 47.8. $C_{14}H_{16}F_{12}N_2O_2$ requires. C, 35.6; H, 3.4; N, 5.9; F, 48.3%), which was identified by a consideration of its i.r. (p. 234), n.m.r. (p. 251), and mass (p. 280) spectra, and shown by ^{19}F n.m.r. spectroscopy to be a mixture of diastereoisomers.

As the reaction was exothermic, it was repeated at

-78 °C to help dissipate the heat of reaction. This gave a colourless mixture, the composition of which was virtually identical to that obtained in the previous reaction.

17a. With norbornadiene (neat reactants)

When a neat oxyl/norbornadiene reaction mixture was allowed to warm up from -196 °C to room temperature extensive charring occurred which resulted in the formation of a black mixture. Hence, the conditions were modified in the following manner.

The oxyl (6) (1.72g, 10.2mmol) and norbornadiene (0.58g, 6.3mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and maintained at -64 °C (2h). The products were separated by condensation *in vacuo* into the following fractions. (a) A fraction which condensed below -23 °C (0.60g), and was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine, carbon dioxide, and unchanged norbornadiene and was not investigated further. (b) A light brown liquid (1.70g), which was shown by g.l.c. (2m KEL F at 95 °C) to contain nine major components (A-I) in the ratio 21.3: 15.5: 13.6: 7: 5: 2·5:1·3:1·1: 1, and *ca.* six minor components which were not present in sufficient quantities to allow their separation and identification.

By a comparison of the retention time of component (A) with that of a known pure sample, it was identified as unchanged norbornadiene (0.18g, 2.0mmol, 32% recovered).

Components (B) and (C) were separated by preparative-scale g.l.c. (as above) to afford the diastereoisomers 2-exo-3-endo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene

$(CF_3)_2NOCHCHON(CF_3)_2CHCH{:}CHCHCH_2$ (A) (0.60g, 1.4mmol, 32%) (Found: C, 30.0; H, 1.9; N, 6.6; F, 53.8. $C_{11}H_8F_{12}N_2O_2$ requires C, 30.8; H, 1.9; N, 6.5; F, 53.3%), and 2-exo-3-exo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene (B) (0.4g, 1.2mmol, 28%) (Found: C, 30.5; H, 2.2; N, 6.5; F, 53.6%), which were identified by a consideration of their i.r. (p. 235), n.m.r. (p. 252,253), and mass (p. 283) spectra.

On the basis of coupled g.l.c. (as above)/mass spectrometry (p. 284), components (D) and (E) were tentatively identified as endo-exo- and exo-exo-2,6-bis(NN-bistrifluoromethylamino-oxy)nortricyclane $(CF_3)_2NOCHCHCHCHCHON(CF_3)_2CHCH_2$, and components (F-I) were tentatively identified as diastereoisomers of 2-exo-3,5,6-tetrakis(NN-bistrifluoromethylamino-oxy)norbornane $(CF_3)_2NOCHCHON(CF_3)_2CHCHON(CF_3)_2CHON(CF_3)_2CHCH_2$; the mass spectra (p. 285) of components (F-I) were virtually identical.

17b. With norbornadiene in solution

To help dissipate the heat of reaction, the oxyl (6) (3.65g, 21.7mmol) and norbornadiene (1.02g, 11.1mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) with 1,1,2-trichloro-1,2,2-trifluoroethane (12.1g) and maintained at -78 °C (40min). The volatile material was removed by condensation in vacuo and the remaining colourless non-volatile liquid was shown by g.l.c. (as above) to contain components (B-I) (as obtained in the previous reaction) in the ratio 7.1: 8.9: 2.2: 2.0: 3.5: 1.1: 1.0: 1.0.

17c. With a large excess of norbornadiene (in solution)

The oxyl (6) (0.6g, 3.6mmol) and norbornadiene (6.22g, 67.5mmol) were sealed in vacuo with 1,1,2-trichloro-1,2,2-trifluoroethane (14.2g) in a Pyrex ampoule (ca. 100cm^3) and maintained at -64 °C (1.5h). Condensation of the products in vacuo gave (a) a volatile fraction (20.34g), which was not investigated, and (b) a colourless non-volatile liquid (0.62g), which was shown by g.l.c. (as above) to contain components (B-E) in the ratio 5.1: 4.8: 1.1: 1.0, and ca. six very minor components. Components (F-I) were not detected amongst the products.

A white solid residue (ca. 0.03g) was also obtained and this was not investigated further.

17d. With norbornadiene (in the gas phase)

The oxyl (6) (3.45g, 20.5mmol) and norbornadiene (1.0g, 10.9mmol) were sealed in vacuo in a Pyrex ampoule (ca. 10dm^3). The reaction was virtually instantaneous (as seen by the immediate disappearance of oxyl colour and the formation of a vapour which slowly condensed on the walls of the bulb).

The light yellow, non-volatile liquid which was drained from the reaction bulb was shown by g.l.c. (as above) to contain components (B-E) in the ratio 1.3: 1.0: 2.0: 1.4, and ca. eleven very minor components. Components (F-I) were not detected amongst the products.

18. With cis-cis-cyclo-octa-1,5-diene

The oxyl (6) (2.58g, 15.4mmol) and cis-cis-cyclo-octa-1,5-diene (0.89g, 8.2mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3). The reaction reached completion as the

mixture warmed up from -196 °C to room temperature. Condensation of the products *in vacuo* gave (a) a volatile fraction, shown by i.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (1.13g, 6.7mmol, 43.5% based on oxyl), and (b) a colourless non-volatile liquid (2.34g), which was shown by g.l.c. (2m TXP at 150 °C) to contain six major components (A-F) in the ratio 1.0: 1.2: 1.1: 1.2: 2.4: 4.3, and *ca.* five minor components which were not present in sufficient quantities to allow their separation and identification.

The major components were separated by preparative-scale g.l.c. (2m SE 30 at 140 °C) and gave the following. (i) Unchanged cyclo-octadiene (F) (0.31g, 2.9mmol, 35% recovered). (ii) 3-(NN-bistrifluoromethylamino-oxy)cyclo-octa-1,5-diene (E) $(CF_3)_2NOCHCH{:}CHCH_2CH_2CH{:}CHCH_2$ (0.44g, 1.6mmol, 30%) (Found: C, 43.4; H, 4.0; N, 5.1. $C_{10}H_{11}F_6NO$ requires C, 43.6; H, 4.0; N, 5.1%), b.p. 179 °C, which was identified by a consideration of its i.r. (p. 235), n.m.r. (p. 253) and mass (p. 286) spectra. (iii) A mixture of components (A) and (B) (*ca.* 1:1) (combined yield *ca.* 0.66g, *ca.* 1.5mmol, *ca.* 28%) (Found: C, 32.5; H, 2.3; N, 6.3; F, 51.9%), which were identified as a bis(NN-bistrifluoromethylamino-oxy)cyclo-octadiene (Calc. for $C_{12}H_{10}F_{12}N_2O_2$: C, 32.6; H, 2.3; N, 6.3; F, 51.6%) and a bis(amino-oxy)cyclo-octene (Calc. for $C_{12}H_{12}F_{12}N_2O_2$: C, 32.4; H, 2.7; N, 6.3; F, 51.4%), by a consideration of the mass spectrum (p. 287) of the two-component mixture. (iv) A mixture of components (C) and (D) (*ca.* 1:1) (combined yield *ca.* 0.66g, *ca.* 1.5mmol, *ca.* 28%) (Found: C, 32.9; H, 2.2; N, 6.6; F, 51.5%), which were identified as a bis(amino-oxy)cyclo-octene and a bis(amino-

oxy)cyclo-octadiene on the basis of the mass spectrum (p. 288) of the two-component mixture. The i.r. spectra of fractions (iii) and (iv) showed absorptions characteristic of an amino-oxy group together with bands in the regions 3.29-3.51 (C-H str.) and ca. 6.06 (C:C str.)μm. The ^{1}H n.m.r. spectra of both fractions showed broad complex absorptions at δ ca. 1.0-2.6 (12H), ca. 4.2 (2H), ca. 4.6-5.0 (2H), and ca. 5.2-5.8 (6H) p.p.m., while the ^{19}F spectra showed several overlapping absorptions at δ ca. 28.8 p.p.m.

19. With cyclo-octene

The oxyl (6) (1.76g, 10.5mmol) and cyclo-octene (0.64g, 5.8mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and reacted as the mixture warmed up from -196 °C to room temperature. Condensation of the products in vacuo gave (a) a -78 °C fraction, which was shown by i.r. spectroscopy to be NN-bistrifluoromethylhydroxylamine (0.17g, 1.0mmol, 10% based on oxyl), and (b) a colourless non-volatile liquid (2.23g), which was shown by g.l.c. (2m SE 30 and APL at 130 °C) to contain three major components (A-C), which were separated by preparative-scale g.l.c. (2m SE 30 at 130 °C) to give (i) unchanged cyclo-octene (0.12g, 1.1mmol, 18% recovered), (ii) 3-(NN-bistrifluoromethylamino-oxy)cyclo-oct-1-ene $(CF_3)_2NO\overline{CHCH:CHCH_2CH_2CH_2CH_2CH_2}$ (0.26g, 0.9mmol, 20%) (Found: C, 42.3; H, 4.4; N, 5.2. $C_{10}H_{13}F_6NO$ requires C, 43.3; H, 4.7; N, 5.0%), b.p. 175-176 °C, which was identified by a consideration of its i.r. (p. 237), n.m.r. (p. 255), and mass (p. 290) spectra, and (iii) 1,2-bis(NN-bistrifluoromethylamino-oxy)cyclo-octane $(CF_3)_2NO\overline{CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2}ON(CF_3)_2$

(1.43g, 3.2mmol, 67.5%) (Found: C, 32.1; H, 3.2; N, 6.0; F, 51.5. $C_{12}H_{14}F_{12}N_2O_2$ requires C, 32.3; H, 3.1; N, 6.3; F, 51.1%), b.p. 200 °C, which was identified by a consideration of its i.r. (p. 237), n.m.r. (p. 255), and mass (p. 290) spectra.

20. With allylbenzene

Experiment 1.

The oxyl (6) (1.96g, 11.7mmol) and allylbenzene (0.56g, 4.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and the reaction reached completion as the mixture warmed up from -196 °C to room temperature. Condensation of the products in vacuo gave (a) a volatile fraction (0.70g), which was shown by i.r. and n.m.r. spectroscopy to consist of NN-bistrifluoromethylhydroxylamine (0.64g, 3.8mmol, 32% based on oxyl) and NN-bistrifluoromethylamine (ca. 0.05g, ca. 0.3 mmol, ca. 2.5% based on oxyl), and (b) a light yellow non-volatile liquid (1.82g), which was shown by g.l.c. (2m TXP and APL at 150 °C) to contain nine components (A-I) in the ratio 2.3: 10.6: 1.0: 5.2: 2.2: 19.3: 10.7: 2.1: 8.6. By a comparison of the retention time of component (G) with that of a known pure sample it was identified as unchanged allylbenzene (ca. 0.09g, ca. 0.8mmol, ca. 17% recovered).

Components (B), (D), (F), and (I) were separated by preparative-scale g.l.c. (4m TXP at 130 °C) to afford (i) 1,2,3-tri(NN-bistrifluoromethylamino-oxy)-3-phenylpropane $(CF_3)_2NOCH_2CHON(CF_3)_2CHPhON(CF_3)_2$, diastereoisomer 1 (B) (0.5g, 0.8mmol, 20.5%) (Found: C, 28.7; H, 1.1; N, 7.0; F, 54.7. $C_{15}H_9F_{18}N_3O_3$ requires C, 29.0; H, 1.4; N, 6.8; F,

55.1%), which was identified by a consideration of its i.r. (p. 238), n.m.r. (p. 256), and mass (p. 292) spectra, (ii) diastereoisomer 2 (D) (0.25g, 0.4mmol, 10%), which was identified by a consideration of its n.m.r. (p. 256) and mass (p. 292) spectra, (iii) 3-(NN-bistrifluoromethylamino-oxy)-3-phenylpropene $(CF_3)_2NOCHPhCH:CH_2$ (F) (0.41g, 1.4mmol, 37%) (Found: C, 46.6; H, 3.2; N, 5.2; F, 40.1. $C_{11}H_9F_6NO$ requires C, 46.3; H, 3.2; N, 4.9; F, 40.0%), b.p. 173 °C, which was identified by a consideration of its i.r. (p. 237), n.m.r. (p. 255), and mass (p. 291) spectra, and (iv) trans-3-(NN-bistrifluoromethylamino-oxy)-1-phenylpropene $(CF_3)_2NOCH_2CH:CHPh$ (I) (0.18g, 0.6mmol, 16.5%) (Found: C, 46.6; H, 3.1; N, 4.9; F, 40.3%), m.p. 32-34 °C, which was identified by a consideration of its i.r. (p. 238), n.m.r. (p. 257), and mass (p. 291) spectra. The minor components (A), (C), (E), and (H) were not identified.

Experiment 2.

The reaction was repeated using a higher molar ratio of oxyl:allylbenzene, i.e. the oxyl (6) (3.12g, 18.6mmol) and allylbenzene (0.51g, 4.3mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and maintained at room temperature (20min). Condensation of the products in vacuo gave (a) a volatile fraction (1.08g), which was shown by i.r. and n.m.r. spectroscopy to consist of NN-bistrifluoromethylhydroxylamine (0.88g, 5.2mmol, 28% based on oxyl) and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (ca. 0.13g, ca. 0.4mmol, ca. 2% based on oxyl), and (b) a light yellow non-volatile liquid (2.55g), which was shown by g.l.c. (2m TXP and APL at 150 °C)

to contain components (B-F) (as obtained in the previous reaction), and a new component (J) in the ratio 20.8: 1.0: 9.6: 1.1: 10.8: 1.5. Components (A), (G), (H), and (I) were not detected in the products of this reaction.

The i.r. spectrum of the mixture showed a weak absorption in the region 5.81-6.01 (C:O str.)μm, which was not observed in the previous reaction mixture, indicating that component (J) was possibly an ester.

21. With penta-1,4-diene

When a neat oxyl/diene reaction mixture was allowed to warm up from -196 °C to room temperature a very exothermic reaction occurred which resulted in extensive charring. Hence the conditions were modified in the following manner.

The oxyl (6) (2.67g, 15.9mmol) and penta-1,4-diene (0.59g, 8.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 50cm^3) and maintained at -78 °C (30min). Condensation of the products in vacuo gave (a) a volatile fraction (ca. 1.55g), which was shown by g.l.c. (2m SE 30 at 70 °C) to contain three components (A-C). By comparison of the retention times of components (A) and (B) with those of known pure samples, and by a consideration of their coupled g.l.c. (as above)/i.r. and mass spectra, they were identified as unchanged penta-1,4-diene (ca. 0.27g, ca. 3.9mmol, ca. 44% recovered), and NN-bistrifluoromethylhydroxylamine (ca. 0.8g, ca. 4.8mmol, ca. 30% based on oxyl).

Component (C) was separated by preparative-scale g.l.c. (as above), contaminated with hydroxylamine, and was tentatively identified as 3-(NN-bistrifluoromethylamino-oxy)-

penta-1,4-diene $CH_2{:}CHCH\left[ON(CF_3)_2\right]CH{:}CH_2$ (0.30g, 1.3mmol, 26.5%) by a consideration of the n.m.r. spectrum (p.258) of the two component mixture, and a coupled g.l.c./mass spectrum (p.116), and (b) a colourless non-volatile liquid (1.71g), which was shown by g.l.c. (as above) to contain four components (D-G) in the ratio 8.2: 2.0: 1.0: 19.3. Component (G) was separated by preparative-scale g.l.c. (as above) and was identified as 1,2,5-tri(NN-bistrifluoromethylamino-oxy)-pent-3-ene $(CF_3)_2NOCH_2CH\left[ON(CF_3)_2\right]CH{:}CHCH_2ON(CF_3)_2$ (1.22g, 2.1mmol, 44.5%) (Found: C, 23.2; H, 1.1; N, 7.4; F, 60.7. $C_{11}H_7F_{18}N_3O_3$ requires C, 23.1; H, 1.2; N, 7.4; F, 59.9%), b.p. 185 °C, by a consideration of its i.r. (p. 238), n.m.r. (p. 257), and mass (p. 293) spectra.

On the basis of coupled g.l.c. (as above)/mass spectrometry (p. 295), component (E) was tentatively identified as 4,5-bis-(NN-bistrifluoromethylamino-oxy)pent-1-ene $(CF_3)_2NOCH_2CH\left[ON(CF_3)_2\right]CH_2CH{:}CH_2$ (ca. 0.06g, ca. 0.1mmol, ca. 2.5%). The coupled g.l.c./mass spectra of components (D) and (F) were identical to those obtained for components (C) and (G), respectively, and they were thus considered to be 1-(NN-bistrifluoromethylamino-oxy)penta-2,4-diene $(CF_3)_2NOCH_2CH{:}CHCH{:}CH_2$ (ca. 0.2g, ca. 0.9mmol, ca. 19%), and a tri(amino-oxy)-substituted adduct (ca. 0.1g, ca. 0.2mmol, ca. 5%), respectively.

A third reaction, using a 2:1 molar mixture of the oxyl and the diene in a Pyrex bulb (ca. 10dm^3), gave a product mixture virtually identical to that obtained in the second reaction.

The reactions of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (7)

1. With t-butyl bromide

The oxadiazapentane (7) (1.82g, 5.7mmol) and t-butyl bromide (0.81g, 5.9mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 300cm^3) and stored at room temperature (15d). Fractional condensation of the products *in vacuo* gave (a) a -196 °C fraction (*ca.* 0.11g, 0.7mmol), which was shown by i.r. spectroscopy to be NN-bistrifluoromethylamine (*ca.* 12% based on oxadiazapentane), (b) a -78 °C fraction (1.64g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine, NN-bistrifluoromethylhydroxylamine and a compound which showed a strong absorption in the region 3.39-3.42 (C-H str.)μm, and (c) a colourless non-volatile liquid (0.88g), which contained a droplet of dark brown liquid (possibly bromine).

The combined fractions (b) and (c) were shown by g.l.c. (2m SE 30 and KEL F at 90 °C) to contain unchanged t-butyl bromide (0.2g, 1.5mmol, 27% recovered), 1,2-dibromo-2-methylpropane (0.3g, 1.4mmol, 32%) and 1-(NN-bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane (see p. 178) (*ca.* 0.08g, *ca.* 0.3mmol, *ca.* 6%), which were identified by a comparison of their retention times with those of known pure samples, and *ca.* thirteen unidentified products which were not investigated further due to the inadequate separation obtained on the g.l.c. columns.

2. With 2-chloro-2-phenylpropane

The oxadiazapentane (7) (2.78g, 8.7mmol) and 2-chloro-2-phenylpropane (1.49g, 9.6mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and stored at room temperature (5d). Fractional condensation of the products *in vacuo* gave (a) a -196 °C fraction (0.24g; M, 74), which was shown by i.r. spectroscopy to consist of hydrogen chloride (*ca.* 0.07g, 1.9mmol, 33% based on consumed chloride), and NN-bistrifluoromethylamine (0.16g, 0.9mmol, 13% based on consumed oxadiazapentane), (b) a -78 °C fraction (1.14g), which was shown by i.r. and n.m.r. spectroscopy to contain unchanged oxadiazapentane (0.64g, 2.0mmol, 23% recovered), and NN-bistrifluoromethylhydroxylamine (0.44g, 2.6mmol, 39% based on consumed oxadiazapentane), and (c) a black non-volatile liquid (2.89g), which was shown by g.l.c. (2m TXP and APL at 150 °C) to be a complex mixture of *ca.* thirteen components, one of which was identified by a comparison of its retention time with that of a known pure sample as unchanged 2-chloro-2-phenylpropane (0.60g, 3.8mmol, 40% recovered) (which decomposes to α-methylstyrene at 150 °C on the g.l.c. column). The mixture was not investigated further.

3. With 3,3,3-trichloropropene

The oxadiazapentane (7) (2.24g, 7.0mmol) and 3,3,3-trichloropropene (1.0g, 6.9mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 100cm^3) and stored at room temperature (20h). Condensation of the products *in vacuo* gave the following. (a) A volatile fraction (1.32g), which was shown by i.r. and n.m.r. spectroscopy to contain unchanged oxadiazapentane

(1.31g, 4.0mmol, 57% recovered), and trace amounts of NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine. (b) A colourless non-volatile liquid (1.92g), which was shown by g.l.c. (2m SE 30 at 114 °C) to contain two major components (A) and (B). By comparison of the retention time of component (A) with that of a known pure sample, it was identified as unchanged trichloropropene (0.56g, 3.9mmol, 56% recovered).

Component (B) was separated by preparative-scale g.l.c. (as above) and identified as 1-NN-bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane $(CF_3)_2NCH_2CHClCCl_2ON(CF_3)_2$ (1.3g, 2.8mmol, 93%) (Found: C, 18.4; H, 0.5; Cl, 22.9; N, 6.0; F, 49.1. $C_7H_3Cl_3F_{12}N_2O$ requires C, 18.1; H, 0.6; Cl, 22.6; N, 6.0; F, 49.1%), b.p. 176 °C, by a consideration of its i.r. (p. 228), n.m.r. (p. 244), and mass (p. 263) spectra.

In an attempt to verify the structure, the adduct (2.9g, 0.6mmol) was refluxed (5h) with concentrated sulphuric acid ($6cm^3$) until the evolution of hydrogen chloride had ceased. The mixture was then added to ice/water (18g) and continuously extracted with diethyl ether ($15cm^3$). The organic layer was then dried ($MgSO_4$) and the ether removed by condensation in vacuo to give a brown tar which was not investigated further.

4. With 3,3,3-trichloro-2-methylpropene

The 3,3,3-trichloro-2-methylpropene (p.176) used in the following reaction was only 90% pure, the contaminant being 1,1,3-trichloro-2-methylpropene.

The oxadiazapentane (7) (2.62g, 8.2mmol) and the

trichloropropene (1.37g, 8.6mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 300cm^3) and stored at room temperature (8d). Condensation of the products *in vacuo* gave the following. (a) A volatile fraction (0.50g), which was shown by i.r spectroscopy to contain *NN*-bistrifluoromethylhydroxylamine, *NN*-bistrifluoromethylamine, and hydrogen chloride and was not investigated further. (b) A colourless non-volatile liquid (3.49g), which was shown by g.l.c. (2m APL at 100 °C) to contain *ca.* ten components.

The two major components were separated by preparative-scale g.l.c. (as above) to afford (i) *1-NN-bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2-methyl-2,3,3-trichloropropane* $(CF_3)_2NCH_2CMeClCCl_2ON(CF_3)_2$ (2.32g, 4.9mmol, 57%) (Found: C, 20.3; H, 1.2; N, 6.1; F, 47.8. $C_8H_5Cl_3F_{12}N_2O$ requires C, 20.0; H, 1.0; N, 5.8; N, 47.5%), which was identified by a consideration of its i.r. (p. 229), n.m.r. (p. 244), and mass (p. 268) spectra, and (ii) a compound shown by g.l.c. analysis (as above) to be contaminated with a minor unidentified component, and which was tentatively identified as 1-(*NN*-bistrifluoromethylamino-oxy)-2-methyl-1,1,2,3-tetrachloropropane $(CF_3)_2NOCCl_2CMeClCH_2Cl$ (0.36g, 1.0mmol, 11.5%) by a consideration of the n.m.r. spectrum (p. 244) of the two-component mixture, and by its coupled g.l.c. (as above)/mass spectrum (p. 269).

The minor components were not identified.

5. *With t-butylbenzene*

The oxadiazapentane (7) (2.0g, 6.3mmol) and *t*-butyl benzene (0.86g, 6.4mmol) were sealed *in vacuo* in a Pyrex

ampoule (ca. 100cm^3) and stored at room temperature (7d). Condensation of the products in vacuo gave the following. (a) A volatile fraction (0.77g), which was shown by i.r. and n.m.r. spectroscopy to contain unchanged oxadiazapentane (0.25g, 0.8mmol, 12% recovered), NN-bistrifluoromethylamine (ca. 0.08g, 0.5mmol, 9% based on consumed oxadiazapentane), and NN-bistrifluoromethylhydroxylamine (0.44g, 2.6mmol, 47% based on consumed oxadiazapentane). (b) A colourless non-volatile liquid (2.09g), which was shown by g.l.c. (2m TXP and APL at 150 °C) to contain six components (A-F) in the ratio 3.7: 1.0: 1.4: 7.0: 8.8: 12.3. By a comparison of the retention time of component (F) with that of a known pure sample, it was identified as unchanged t-butylbenzene (0.31g, 2.3mmol, 36% recovered).

Components (E), (D), and (A) were separated by preparative-scale g.l.c. (4m TXP at 140 °C) to give (i) 4-(NN-bistrifluoromethylamino)-t-butylbenzene (E) $(CF_3)_2NC_6H_4CMe_3$ (0.47g, 1.6mmol, 40%) (Found: C, 50.3; H, 4.8; N, 4.7; F, 40.2. $C_{12}H_{13}F_6N$ requires C, 50.5; H, 4.6; N, 4.9; F, 40.0%), which was identified by a consideration of its i.r. (p. 229), n.m.r. (p. 245), and mass (p. 271) spectra, (ii) a second isomer tentatively identified as 3-(NN-bistrifluoromethylamino)-t-butylbenzene (D) $(CF_3)_2NC_6H_4CMe_3$ (0.37g, 1.3mmol, 31.5%) (Found: C, 50.7; H, 4.7; N, 5.0%) by a consideration of its i.r. (p. 230), n.m.r. (p. 245), and mass (p. 271) spectra, and (iii) a bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)-t-butylcyclohexene (A) (0.54g, 0.7mmol, 17%) (Found: C, 28.1; H, 1.7;

N, 8.0. $C_{18}H_{14}F_{24}N_4O_2$ requires C, 27.9; H, 1.8; N, 7.2%), which was identified by a consideration of its i.r. (p. 230), n.m.r. (p. 259), and mass (p. 272) spectra, and shown by n.m.r. spectroscopy to be a mixture of isomers.

Components (B) and (C) were not present in sufficient quantities to allow their separation and identification.

6. With 2-phenylpropan-2-ol

The oxadiazapentane (7) (2.14g, 6.7mmol) and 2-phenylpropan-2-ol (0.82g, 6.0mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (18d). The products were separated by condensation in vacuo into the following. (a) A fraction which condensed below -23 °C (0.1g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine, and NN-bistrifluoromethylhydroxylamine and was not investigated further. (b) A light brown liquid (2.8g), which was shown by g.l.c. (2m APL and SE 30 at 185 °C) to contain ca. eleven lower-boiling components, and three high-boiling components (A-C) (combined yield ca. 10% based on alcohol), which were identified as isomeric dimers of α-methylstyrene by a comparison of their retention times with the three high-boiling components obtained in the reaction of 2-phenylpropan-2-ol with NN-bistrifluoromethylhydroxylamine (see p. 224); the products could not be effectively separated by g.l.c. and the fraction was not investigated further. (c) A white solid (ca. 0.05g), which remained in the reaction tube and was not investigated further.

7. With cyclopropylcarbinol

The oxadiazapentane (7) (3.16g, 9.9mmol) and cyclopropylcarbinol (0.70g, 9.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (18d). Fractional condensation of the products in vacuo gave (a) a -196 °C fraction, which was shown by i.r. spectroscopy to be NN-bistrifluoromethylamine (1.1g, 7.2mmol, 73% based on oxadiazapentane), (b) a -78 °C fraction (0.8g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine, and was not investigated further, and (c) a dark brown non-volatile liquid (1.95g), which was shown by g.l.c. (2m SE 30 at 120 °C) to be a complex mixture of ca. eight lower-boiling and ca. sixteen higher-boiling components.

The i.r. spectrum of fraction (c) showed strong absorptions in the region 5.62-5.95 (C:O str.)μm, together with O-H absorptions, indicating that oxidation had occurred to some extent.

8. With cyclopropylmethylcarbinol

The oxadiazapentane (7) (2.9g, 9.1mmol) and cyclopropylmethylcarbinol (0.81g, 9.4mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (7d). Fractional condensation of the products in vacuo gave (a) a -196 °C fraction, which was shown by i.r. spectroscopy to be NN-bistrifluoromethylamine (0.72g, 4.7mmol, 52% based on oxadiazapentane), (b) a -78 °C fraction (0.24g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine and which

was not investigated further, (c) a -23 °C fraction (0.3g), which was combined with (d) a light brown non-volatile liquid (2.45g).

The mixture of fractions (c) and (d) was shown by g.l.c. (2m SE 30 at 100 °C) to be a complex mixture of ca. eleven lower-boiling, and ca. eleven higher-boiling components, one of which was identified as unchanged cyclopropylmethylcarbinol (ca. 0.04g, ca. 0.5mmol, ca. 18% recovered), by a comparison of its retention time with that of a known pure sample.

The i.r. spectrum of the mixture showed strong absorptions in the region 5.65-5.95 (C:O str.)μm, together with a broad O-H absorption, indicating that oxidation of the alcohol had occurred to some extent.

9. With cyclopropylphenylmethane

The oxadiazapentane (7) (2.71g, 8.5mmol) and cyclopropylphenylmethane (1.09g, 8.3mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and kept at room temperature (1d). Condensation of the products in vacuo gave (a) a volatile fraction (1.54g), which was shown by i.r. and n.m.r. spectroscopy to contain unchanged oxadiazapentane (1.4g, 4.5mmol, 53% recovered), NN-bistrifluoromethylamine (0.15g, 1.0mmol, 25% based on consumed oxadiazapentane), and NN-bistrifluoromethylhydroxylamine (trace), and (b) a colourless non-volatile liquid (2.26g), which was shown by g.l.c. (2m APL at 150 °C) to contain one major component and ca. nineteen minor components. The major component was identified by coupled g.l.c. (as above)/mass spectrometry and

by a comparison of its retention time with that of a known pure sample as unchanged cyclopropylphenylmethane (0.53g, 4.0mmol, 48% recovered). The minor components were investigated by coupled g.l.c./mass spectrometry but the results were rather ambiguous and it was difficult to assign structures; several components showed base peaks at m/e 91, with a parent ion at m/e 283, and on this evidence they have been tentatively identified as bistrifluoromethylamino-substituted cyclopropanes of general formulae $PhCH_2C_3H_4N(CF_3)_2$.

10. With 2(10)-pinene (β-pinene)

The oxadiazapentane (7) (3.06g, 9.6mmol) and 2(10)-pinene (1.12g, 8.2mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and stored at room temperature (6d). Condensation of the products in vacuo gave (a) a volatile fraction (0.58g), which was shown by i.r. spectroscopy to consist mainly of NN-bistrifluoromethylamine, and NN-bistrifluoromethylhydroxylamine and was not investigated further, and (b) a colourless non-volatile liquid (3.6g), which was shown by g.l.c. (2m TXP and SE 30 at 150 °C) to contain ca. eleven components (both columns showed six overlapping peaks).

Separation of certain of the components by preparative-scale g.l.c. (4m SE 30 followed by 2m APL at 140 °C) gave (i) a mixture of two components (in the ratio ca. 2:1) tentatively identified as 10-(NN-bistrifluoromethylamino)-2-pinene $(CF_3)_2NCH_2\overline{C:CHCH_2\underline{CHCH_2}CHCMe_2}$ (ca. 0.35g, ca. 1.2 mmol, ca. 15%) and 10-(NN-bistrifluoromethylamino-oxy)-2-pinene $(CF_3)_2NOCH_2\overline{C:CHCH_2\underline{CHCH_2}CHCMe_2}$ (ca. 0.17g, ca. 0.6mmol, ca. 7%), by a consideration of the i.r. (p. 234), n.m.r. (p. 251), and mass (p.281)spectra of the two-component

mixture, (ii) a component tentatively identified as 1-(NN-bistrifluoromethylamino)methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene $(CF_3)_2NCH_2\overline{C:CHCH_2CH[CMe_2ON(CF_3)_2]CH_2CH_2}$ (ca. 0.37g, ca. 0.8 mmol, ca. 10%) (Found: C, 38.1; H, 4.0; N, 5.9. $C_{14}H_{16}F_{12}N_2O$ requires C, 36.8; H, 3.5; N, 6.1%), on the basis of its n.m.r. (p. 252) and mass (p. 276) spectra, and (iii) a component tentatively identified as 1-(NN-bistrifluoromethylamino)methyl-4-isopropylcyclohex-1-ene $(CF_3)_2NCH_2\overline{C:CHCH_2CH(CHMe_2)CH_2CH_2}$ (ca. 0.47g, ca. 1.6mmol, ca. 20%) (Found: C, 48.4; H, 6.0; N, 4.3. $C_{12}H_{17}F_6N$ requires C, 49.8; H, 5.9; N, 4.8%), by a consideration of its n.m.r. (p. 252) and mass (p.282) spectra.

11. With 2-pinene (α-pinene)

The oxadiazapentane (7) (2.54g, 7.9mmol) and 2-pinene (1.05g, 7.7mmol) were sealed in vacuo in a Pyrex ampoule (ca. 300cm^3) and stored at room temperature (15d). Consensation of the products in vacuo gave (a) a volatile fraction (0.66g), which was shown by i.r. and n.m.r. spectroscopy to be mainly NN-bistrifluoromethylamine (ca. 0.28g, ca. 1.8mmol, ca. 23% based on oxadiazapentane) and NN-bistrifluoromethylhydroxylamine (ca. 0.29g, ca. 1.7mmol, ca. 22% based on oxadiazapentane) contaminated with a small amount of an unidentified component which showed an absorption in the ^{19}F n.m.r. spectrum at δ -11.5 p.p.m. (w.r.t. T.F.A. reference), and (b) a colourless non-volatile liquid (2.93g), which was shown by g.l.c. (2m APL and SE 30 at 135 °C) to be a complex mixture of ca. fourteen components which could not be

adequately separated, and which were not investigated further.

12. With norbornadiene

The oxadiazapentane (7) (2.84g, 8.9mmol) and norbornadiene (0.82g, 8.9mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (5d). The products were seen to have formed an upper layer of yellow/brown solid material and a lower layer of yellow liquid.

Hence, the reaction was repeated in solution using the oxadiazapentane (7) (3.46g, 10.8mmol) and norbornadiene (0.9g, 9.8mmol) which were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) with 1,1,2-trichloro-1,2,2-trifluoroethane (7.25g) and stored at room temperature (8d). The lower-boiling material was removed by condensation in vacuo and the remaining non-volatile gelatinous material (ca. 4.0g) (Found: C, 33.4; H, 2.1; N, 4.9; F, 49.4%) was tentatively identified on the basis of its mass spectrum (p.297) as a mixture of telomeric products of general formulae $(CF_3)_2N[C_7H_8]_xON(CF_3)_2$ (where x= 1,2,...). The i.r. and n.m.r. spectra of the mixture were very complex and of little help in the identification of the products. Attempts to separate the gelatinous material by column chromatography and t.l.c. (using chloroform, acetone and 1,1,2-trichloro-1,2,2-trifluoroethane as eluants) proved unsuccessful.

The non-volatile material was therefore dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane (3x10cm^3) and the solvent removed by condensation in vacuo in an attempt to

remove the residual lower-boiling material. This gave a white solid (ca. 3.5g) (Found: C, 42.4: H, 3.6; N, 5.5; F, 49.3%). The i.r. and n.m.r. spectra of the solid were very complex and showed only that it contained NN-bistrifluoromethylamino- and NN-bistrifluoromethylamino-oxy groups, and was not investigated further.

13. With cis-cis-cyclo-octa-1,5-diene

The oxadiazapentane (7) (3.69g, 11.5mmol) and cis-cis-cyclo-octa-1,5-diene (1.29g, 11.9mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (6d). Condensation of the products in vacuo gave the following. (a) A volatile fraction (0.71g), which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine and was not investigated further. (b) A colourless non-volatile liquid (4.26g), which was shown by g.l.c. (2m SE 30 and TXP at 150 °C) to contain eight components (A-H). By a comparison of the retention time of component (A) with that of a known pure sample it was identified as unchanged cyclo-octadiene (0.13g, 1.2mmol, 10% recovered).

The three major components (F-H) were separated by preparative-scale g.l.c. (2m SE 30 followed by 2m TXP at 125 °C) to afford (i) 1-NN-bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)cyclo-oct-5-ene $(CF_3)_2N\overline{CHCH_2CH_2CH:CHCH_2CH_2}CHON(CF_3)_2$, diastereoisomer 1 (G) (1.55g, 3.6mmol, 34%) (Found: C, 33.7; H, 2.9; N, 6.8; F, 53.8. $C_{12}H_{12}F_{12}N_2O$ requires C, 33.6; H, 2.8; N, 6.5; F, 53.3%), which was identified by a consideration of its i.r.

(p. 236), n.m.r. (p. 254), and mass (p. 289) spectra, (ii) diastereoisomer 2 (H) (1.24g, 3.0mmol, 28%) (Found: C, 33.8; H, 3.0; N, 6.5%), which was identified by a consideration of its i.r. (p. 236), n.m.r. (p. 254), and mass (p. 289) spectra, and (iii) component (F), which was tentatively identified as an amino-oxy-substituted cyclo-octadiene (ca. 0.39g, ca. 1.4mmol, ca. 13%) by a consideration of its ^{1}H n.m.r. spectrum (ca. 15% in carbon tetrachloride solution) which showed complex absorptions at δ ca. 1.2-2.6 (6H), ca. 5.0 (1H), and ca. 5.5 (4H) p.p.m., and its ^{19}F n.m.r. spectrum which showed a singlet at δ 27.0 p.p.m. Component (C) was partially separated by preparative-scale g.l.c. (as above) and although impure, was tentatively identified as 1-(NN-bistrifluoromethylamino)cyclo-oct-5-ene $(CF_3)_2N\overline{CHCH_2CH_2CH_2CH:CHCH_2CH_2}$ (ca. 0.3g, ca. 0.1mmol, ca. 9%) on the basis of its n.m.r. spectrum (p. 253).

14. With allylbenzene

The oxadiazapentane (7) (2.3g, 7.2mmol) and allylbenzene (0.89g, 7.5mmol) were sealed in vacuo in a Pyrex ampoule (ca. $100cm^3$) and stored at room temperature (6d). Condensation of the products in vacuo gave (a) a volatile fraction (0.27g), which was shown by i.r. and n.m.r. spectroscopy to consist of unchanged oxadiazapentane (0.14g, 0.5mmol, 7% recovered), NN-bistrifluoromethylamine (ca. 0.05g, ca. 0.3mmol, ca. 5%) and NN-bistrifluoromethylhydroxylamine (ca. 0.07g, ca. 0.4 mmol, ca. 6%), and (b) a light yellow non-volatile liquid (2.92g), which was shown by g.l.c. (2m TXP and APL at 150 °C) to contain five major components (A-E) in the ratio 12.5: 1.1: 1.3: 2.3: 1.0, and six minor components which were not

present in sufficient quantities to allow their separation and identification.

Components (C) and (E) were identified, by a comparison of their retention times with those of known pure samples, as unchanged allylbenzene (ca. 0.05g, ca. 0.5mmol, ca. 6% recovered) and trans-3-(NN-bistrifluoromethylamino-oxy)-1-phenylpropene (0.11g, 0.4mmol, 5.5%) (see p. 204).

Component (A), which was separated by preparative-scale g.l.c. (2m APL at 150 °C), was identified as 1-NN-bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)-3-phenylpropane $(CF_3)_2NCH_2CHON(CF_3)_2CH_2Ph$ (2.07g, 4.7mmol, 66.5%) (Found: C, 35.9; H, 2.3; N, 6.5; F, 51.7. $C_{13}H_{10}F_{12}N_2O$ requires C, 35.6; H, 2.3; N, 6.4; F, 52.1%), by a consideration of its i.r. (p. 239), n.m.r. (p.258), and mass (p. 296) spectra.

The higher-boiling components were investigated by coupled g.l.c./mass spectrometry, but adequate separation could not be acheived, and components (B) and (D) were not identified.

15a. With penta-1,4-diene in the gas phase

The oxadiazapentane (7) (3.2g, 10.0mmol) and penta-1,4-diene (0.71g, 10.4mmol) were sealed in vacuo in a Pyrex ampoule (ca. 10dm^3) and kept at room temperature (2d). Analysis of the mixture by g.l.c. (2m SE 30 at 90 °C to 150 °C) showed that it contained unchanged diene (ca. 0.09g, ca. 1.4mmol, ca. 13% recovered), identified by a comparison of its retention time with that of a known pure sample, and one major and ca. twenty minor components. Condensation or

the products *in vacuo* gave the following. (a) A volatile fraction (*ca.* 0.45g), which was shown by i.r. and n.m.r. spectroscopy to contain unchanged penta-1,4-diene, *NN*-bistrifluoromethylamine, and *NN*-bistrifluoromethylhydroxylamine. The ^{19}F n.m.r. spectrum of the mixture showed *ca.* nine absorptions in the region δ -6 to -21 p.p.m. (w.r.t. T.F.A) and was not investigated further. (b) A colourless non-volatile liquid (*ca.* 3.46g), which was shown by g.l.c. (as above) to contain *ca.* fifteen components.

The major component was separated by preparative-scale g.l.c. (as above) and identified as *1-NN-bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)pent-4-ene* $(CF_3)_2NCH_2CHON(CF_3)_2CH_2CH{:}CH_2$ (*ca.* 2.41g, *ca.* 6.2mmol, *ca.* 70%) (Found: C, 27.5; H, 2.2; N, 7.2; F, 58.3. $C_9H_8F_{12}N_2O$ requires C, 27.8; H, 2.1; N, 7.2; F, 58.8%), which was identified by a consideration of its i.r. (p. 239), n.m.r. (p. 259), and mass (p. 296) spectra.

15b. *With penta-1,4-diene (gas and liquid phases present)*

The oxadiazapentane (7) (2.79g, 8.7mmol) and penta-1,4-diene (0.57g, 8.4mmol) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 50cm^3) and kept at room temperature (2d). Analysis by g.l.c. (as above) showed that the mixture contained three major components (A-C) in the ratio 1.7: 1.1: 1.0, and *ca.* eighteen minor components. Component (A) was identified by a comparison of its retention time with that of a known pure sample as 1-*NN*-bistrifluoromethylamino-2-(*NN*-bistrifluoromethylamino-oxy)pent-4-ene (*ca.* 1.07g, *ca.* 2.8mmol, *ca.* 33%). Condensation of the products *in vacuo*

gave the following. (a) A volatile fraction (ca. 0.8g), which was shown by i.r. spectroscopy to contain unchanged penta-1,4-diene, NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine. The ^{19}F n.m.r. spectrum of the mixture showed ca. fifteen absorptions in the region δ -6.0 to -23.0 p.p.m. (w.r.t. T.F.A.) and was not investigated further. (b) A colourless non-volatile liquid (ca. 2.56g), which was shown by g.l.c. (as above) to contain ca. thirteen components.

Components (B) and (C) were separated together (contaminated with several minor unidentified components) by preparative-scale g.l.c. (as above) and were tentatively identified as NN-bistrifluoromethylamino-NN-bistrifluoromethylamino-oxy-substituted dimers of penta-1,4-diene (combined yield ca. 41% based on diene), by a consideration of the mass spectrum (p. 298) of the mixture. The ^{1}H n.m.r. spectrum of the component mixture showed poorly resolved absorptions at δ ca. 1.1-2.0 (4H, c), ca. 2.9 (2H, c), ca. 3.8-4.3 (2H, c), and ca. 4.8-5.7 (3H, c) p.p.m. The ^{19}F n.m.r. spectrum showed absorptions at (i) δ 29.8(s), 29.5 (s) and 28.6 (c) p.p.m., and (ii) δ ca. 19.0 (-19.0) p.p.m., integrated intensities ca. 3:2.

16. With chlorobenzene

The oxadiazapentane (7) (3.66g, 11.4mmol) and chlorobenzene (1.30g, 11.5mmol) were sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and stored at room temperature (7d). Fractional condensation of the products in vacuo gave the following. (a) A -196 ^{o}C fraction (0.14g; M, 100), which

was shown by i.r. spectroscopy to contain hydrogen chloride (ca. 0.02g, ca. 0.16mmol, ca. 8%) and NN-bistrifluoromethylamine [0.11g, 0.7mmol, 7.5 % based on (7)]. (b) A -78 °C fraction (1.45g), which was shown by i.r. and n.m.r. spectroscopy to contain unchanged oxadiazapentane (7) (0.7g, 2.2 mmol, 19% recovered) and NN-bistrifluoromethylhydroxylamine [0.75g, 4.4mmol, 48% based on (7)]. (c) A yellow non-volatile liquid (3.38g), which was shown by g.l.c. (2m TXP at 110 °C) to contain four major components (A-D) in the ratio 1.4: 3.4: 1.0: 4.3, and ca. ten minor components which were not present in sufficient quantities to allow their separation and identification. Component (D) was identified by comparing its retention time with that of a known pure sample as unchanged chlorobenzene (0.47g, 4.1mmol, 36% recovered)

Components (A) and (B) were partially separated by preparative-scale g.l.c. (as above) and tentatively identified as a bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)chlorocyclohexene (A) (1.0g, 1.4mmol, 18%) (Found: C, 24.5; H, 0.5; Cl, 3.5; N, 6.0. Calc. for $C_{14}H_5ClF_{24}N_4O_2$: C, 22.3; H, 0.7; Cl, 4.7; N, 7.4%), on the basis of its i.r. (p. 231) and mass (p. 273) spectra; the ^1H n.m.r. spectrum of the isolated sample showed absorptions at δ 3.3-4.9 (4H, c), and 6.1-6.4 (1H, c) p.p.m., together with an AA'BB' system centred on δ 6.95 p.p.m. and it is considered that the sample contained 4-(NN-bistrifluoromethylamino)chlorobenzene $(CF_3)_2NC_6H_4Cl$ as a contaminant. The ^{19}F n.m.r. spectrum showed absorptions at δ 12.1 (c), 17.35 (s), 29.0 (c), and 29.6 (s) p.p.m., integrated intensities

1: 3: 3: 2.5.

Component (B) was tentatively identified as 2-(NN-bistrifluoromethylamino)chlorobenzene $(CF_3)_2NC_6H_4Cl$ (0.85g, 3.2mmol, 43%) (Found: C, 33.6, 33.0; H, 1.1, 1.1; N, 6.6, 4.3. Calc. for $C_8H_4ClF_6N$: C, 36.4; H, 1.5; N, 5.3%), by a consideration of its i.r. (p. 230), n.m.r. (p. 246), and mass (p. 270) spectra; the ^1H n.m.r. spectrum of the isolated sample showed complex absorptions at δ ca. 3.9-4.6 p.p.m., together with the expected absorption for the nuclear hydrogens in an amino-substituted chlorobenzene, and indicated that the sample was not pure.

The reaction of NN-bistrifluoromethylhydroxylamine with 2-phenylpropan-2-ol

A mixture of NN-bistrifluoromethylhydroxylamine (1.68g, 10.0mmol) and 2-phenylpropan-2-ol (1.34g, 10.0mmol) was sealed in vacuo in a Pyrex ampoule (ca. 100cm^3) and kept at room temperature (1d). Condensation of the products in vacuo gave the following. (a) A volatile fraction (1.84g), which was not fully investigated but which was shown by i.r. spectroscopy to contain NN-bistrifluoromethylhydroxylamine. (b) A yellow non-volatile (1.18g), which did not shown any absorptions in the i.r. spectrum in the region 2.8-3.1 (O-H str.)μm. The liquid was dissolved in diethyl ether (25cm^3) and then shaken with dilute sodium hydroxide solution to remove residual hydroxylamine. The organic layer was separated, dried ($CaSO_4$), and the ether separated by condensation in vacuo. The resulting colourless liquid was shown by g.l.c. (2m PEGA and SE 30 at 190 °C) to contain three major higher-boiling components (A-C) in the ratio

1.0: 1.4: 1.1, and three very minor lower-boiling components.

The i.r. spectrum of the mixture was typical of a non-fluorinated alkene and showed absorptions in the regions 3.25-3.50 (C-H str.), 6.26-6.94 (C:C str.), 8.95-9.73 (C-H def.), and 13.16 and 14.29 (C-H def.)μm. The ^{1}H n.m.r. spectrum of the mixture showed broad absorptions in the regions δ 0.4-1.4, ca. 1.6-2.5, ca. 4.3-4.8, and ca. 6.7 p.p.m., integrated intensities ca. 12: 3: 1: 17. The mass spectrum of the mixture showed peaks at m/e 236 (20%, $C_{18}H_{20}^{+\cdot}$), 221 [67%, $(M-CH_3)^+$], 154 (100%, $C_{12}H_{10}^{+\cdot}$), 143 (22%, $C_{11}H_{11}^+$), 119 (98%, $C_9H_{11}^+$), 91 (53%, $C_7H_7^+$), and 77 (23%, $C_6H_5^+$). On this evidence, the three major components (A-C) were identified as isomeric dimers of α-methylstyrene of general formulae $C_{18}H_{20}$.

APPENDIX A

INFRARED SPECTRA

Band positions are quoted in micrometres followed by the relative intensity of the absorption. (w= weak, m= medium, s= strong, vs=very strong, sh= shoulder, br= broad).

1,2,3-Tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane

$[(CF_3)_2NOCH_2]_2CMeON(CF_3)_2$ (9) liquid

3.31 w(sh); 3.33 w; 3.36 w(sh); 3.38 w; 3.42 w; 3.45 w(sh); 4.12 w(br); 4.67 w; 5.47 w; 6.76 m; 6.84 m; 7.17 m; 7.26 m (sh); 7.29 m; 7.69 vs(br); 7.99 vs(br); 8.30 vs(br); 8.83 m; 9.41 s; 10.35 vs; 11.33 w; 11.98 w; 12.05 w(sh); 12.30 w; 12.69 w; 13.37 w; 14.08 vs, and 14.33 m.

1-(NN-Bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane

$(CF_3)_2NOCH_2CMe_2Br$ (10) liquid

3.36 m; 3.41 m; 3.43 w(sh); 3.47 w(sh); 4.14 w(br); 4.70 w; 5.48 w; 6.79 m; 6.95 m; 7.02 m; 7.19 s; 7.26 s; 7.69 vs(br); 7.99 vs(br); 8.30 vs(br); 8.89 s; 9.09 s; 9.62 s(br); 10.44 vs; 11.42 m; 11.99 m; 12.35 m; 13.05 m, and 14.29 s.

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane $(CF_3)_2NOCH_2CMe(CH_2Br)ON(CF_3)_2$ (11) liquid

3.33 w; 3.34 w(sh); 3.38 w; 3.42 w; 3.45 w; 4.12 w(br); 4.67 w; 6.76 w(sh); 6.82 m; 6.97 w; 7.00 w(sh); 7.18 m; 7.26 m(sh); 7.69 vs(br); 7.97 vs(br); 8.29 vs(br); 8.93 m; 9.40 s(br); 10.32 s; 11.21 w; 11.44 w; 11.74 w(br); 12.12 m; 12.70 w; 13.89 w; 13.62 w; 14.08 vs; 14.29 m, and 14.49 m.

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3-chloro-2-methylpropane $(CF_3)_2NOCH_2CMe(CH_2Cl)ON(CF_3)_2$ (17) liquid

3.33 m; 3.37 m; 3.42 w; 4.11 w(br); 4.66 w; 5.48 m; 6.76 m; 6.82 m; 7.18 m; 7.66 vs(br); 7.97 vs(br); 8.26 vs(br); 8.82 m; 9.05 m; 9.38 s; 9.49 s(sh); 10.31 vs; 11.17 w; 12.06 m; 12.48 m; 12.79 w; 13.07 m; 13.33 m; 13.97 vs, and 14.25 m.

1,2-Bis(NN-bistrifluoromethylamino-oxy)-2-chloropropane $(CF_3)_2NOCH_2CMeClON(CF_3)_2$ (18) liquid

3.33 m; 3.39 m; 3.46 w; 4.14 w(br); 4.69 w; 6.44 w; 6.54 w; 6.81 s; 6.87 m(sh); 7.17 s; 7.63 vs(br); 7.92 vs(br); 8.24 vs(br); 8.64 s; 9.03 s(sh); 9.12 s; 9.36 s(br); 9.54 s; 10.29 s; 11.82 s; 12.20 m(sh); 13.37 m; and 14.03 s.

1,2-Bis(NN-bistrifluoromethylamino-oxy)-2-phenylpropane $(CF_3)_2NOCH_2CPhMeON(CF_3)_2$ (20) liquid

3.22 w(sh); 3.24 w; 3.26 m; 3.30 m; 3.33 m; 3.36 w; 3.38 m; 3.42 w; 3.47 w; 4.12 w(br); 4.67 w; 6.24 w; 6.32 w; 6.49 w; 6.69 m; 6.85 m(sh); 6.92 m; 7.22 m; 7.30 m; 7.72 vs(br); 7.97 vs(br); 8.30 vs(br); 8.87 s; 9.17 m; 9.46 s; 9.69 s; 9.95 m; 10.37 vs; 10.56 m; 10.96 w; 11.85 m; 12.20 m; 12.35 w(sh); 13.04 s; 13.26 m; 13.48 w; 14.12 vs; 14.39 s; 15.04 m; and 15.80 m.

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3,3,3-trichloropropane $(CF_3)_2NOCH_2CH(CCl_3)ON(CF_3)_2$ (22) liquid

3.33 s(sh); 3.36 w; 3.44 w; 4.12 w(br); 4.67 w; 6.49 w; 6.83 m; 7.69 vs(br); 8.29 vs(br); 8.91 m; 9.26 s(sh); 9.42 s; 9.55 s; 10.03 w(sh); 10.35 s; 9.66 w(sh); 10.93 w; 11.11 w; 11.89 s; 12.38 s; 12.66 s; 13.46 m; 14.08 vs; 14.37 m; 14.66 m; 14.99 m(sh); and 15.65 m.

1,3-Bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane $(CF_3)_2NOCH_2CHClCCl_2ON(CF_3)_2$ (23) liquid

3.34 w(sh); 3.37 m; 3.44 w; 4.12 w(br); 4.67 w; 6.83 m; 6.86 w(sh); 6.96 m; 7.20 m; 7.66 vs(br); 7.97 vs(br); 8.29 vs(br); 8.60 s; 9.01 m(sh); 9.35 s(br); 9.52 s(sh); 9.68 s; 10.31 vs; 11.36 m(sh); 12.06 s(sh); 12.24 s; 12.77 m; 13.29 m; 13.42 m; and 13.99 vs.

1-NN-Bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane

$(CF_3)_2NCH_2CHClCCl_2ON(CF_3)_2$ (29) liquid

3.31 w; 3.35 w; 6.85 m; 7.28 vs; 7.46 vs(br); 7.63 vs; 7.96 vs; 8.33 vs(br); 8.53 vs(br); 8.97 vs(br); 9.43 m(sh); 9.57 s(sh); 9.71 s; 10.0 s; 10.38 s(br); 10.82 m; 11.90 m; 12.35 m; 12.63 m; 13.25 m; 14.04 vs; 14.49 m; 14.93 m; and 15.58 m.

1-NN-Bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2-methyl-2,3,3-trichloropropane

$(CF_3)_2NCH_2CMeClCCl_2ON(CF_3)_2$ (30) liquid

3.31 w; 3.34 w; 3.38 w; 3.43 w; 6.83 w; 6.87 w(sh); 7.15 s; 7.28 s; 7.51 vs; 7.63 vs; 7.99 vs; 8.24 vs; 8.35 vs(sh); 8.47 vs(br); 8.59 vs(sh); 8.98 s; 9.14 s; 9.72 s; 10.0 s; 10.24 s(sh); 10.41 s; 11.01 w; 11.36 w; 11.83 m; 12.02 m; 12.17 m; 12.38 m; 12.63 m; 13.32 w; 14.04 s; 14.29 m; and 14.64 m.

1-(NN-Bistrifluoromethylamino-oxy)-2-methyl-2-phenylpropane

$(CF_3)_2NOCH_2CMe_2Ph$ (39) liquid

3.23 m; 3.25 m; 3.27 m; 3.36 s; 3.45 m; 5.51 m; 6.25 m; 6.68 m; 6.78 m; 6.91 m(br); 7.15 m; 7.29 s; 7.72 vs(br); 7.94 vs(br); 8.33 vs(br); 8.49 s; 9.52 vs; 9.90 m; 10.37 vs; 10.81 w; 11.81 w; 11.96 w; 12.42 w; 13.16 vs; 14.20 vs; and 14.45 vs.

4-NN-Bistrifluoromethylamino-t-butylbenzene

$(CF_3)_2NC_6H_4CMe_3$ (40) liquid

3.28 w; 3.38 s; 3.45 m; 3.48 m; 4.74 w; 5.24 w; 6.02 w; 6.64 s; 6.80 m; 6.84 m; 7.19 m; 7.35 vs; 7.46 vs(br); 7.75 vs(br); 8.21 vs; 8.33 s; 8.66 vs(br); 8.93 s; 9.01 s; 9.77 m; 10.22 vs; 10.53 vs, 11.92 s; 12.90 w; 13.30 m; 13.87 s; and 14.25 vs.

3-NN-Bistrifluoromethylamino-t-butylbenzene

$(CF_3)_2NC_6H_4CMe_3$ (41) (tentatively identified) liquid

3.25 w(br); 3.38 s; 3.44 w; 3.48 w; 6.24 m; 6.31 w; 6.72 m; 6.80 w; 7.00 m; 7.17 w; 7.45 vs(br); 7.54 vs; 7.78 vs(br); 8.29 s; 8.64 vs(br); 9.17 w; 10.26 vs; 11.17 w; 11.76 m; 12.5 m; 13.7 m; 13.89 vs; and 14.27 m.

Bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)-t-butylcyclohexene

(mixture of diastereoisomers) liquid

3.36 m; 3.42 w; 3.47 w; 6.76 w; 6.82 w; 7.03 m; 7.49 vs(br); 7.69 vs(br); 8.00 vs(br); 8.30 vs(br); 8.50 vs(br); 8.89 s; 9.59 s; 9.85 m; 10.07 m; 10.35 s; 10.67 w(sh); 11.11 w; 11.24 w(sh); 11.70 w; 12.29 w; 12.47 w; 13.33 w; 13.57 w; 13.81 m; 14.10 s; 14.33 m; and 14.56 m.

2-NN-Bistrifluoromethylaminochlorobenzene

$(CF_3)_2NC_6H_4Cl$ (52) (tentatively identified) liquid

3.25 w; 3.32 w; 5.27 w; 6.08 w; 6.28 w; 6.71 s; 6.85 m; 7.10 m; 7.43 vs(br); 7.87 vs(br); 8.24 vs(br); 8.64 vs(br); 9.01 m; 9.16 s; 9.66 m; 9.82 m; 10.22 vs; 10.38 s; 10.58 s; 12.05 s; 12.27 m; 12.95 m; 13.19 w; 13.35 w; 13.70 s; 13.91 w; 14.12 m; 14.49 s; and 14.51w.

Mixture of bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)chlorocyclohexene and 4-NN-bistrifluoromethylaminochlorobenzene (tentatively identified)

3.23 w(br); 3.39 w(br); 4.12 w(br); 5.29 w; 6.08 w; 6.25 m; 6.68 s; 6.83 w; 7.03 m; 7.43 vs(br); 7.69 vs(br); 8.00 vs; 8.26 vs(br); 8.65 vs; 8.98 s; 9.07 s(sh); 9.61 s; 9.97 m; 10.22 s; 10.35 s; 10.55 s; 11.24 m; 11.93 m; 12.20 m; 13.40 m; 13.62 s; 13.89 s; 14.10 s; and 14.45 s.

1,1-Dimethyl-2-(NN-bistrifluoromethylamino-oxy)-2-oxoethyl acetate $(CF_3)_2NOCOCMe_2OAc$ (59) liquid

3.33 m; 3.39 w; 3.45 w; 5.47 s; 5.71 s; 6.79 m; 6.86 m; 6.94 m; 7.03 w(sh); 7.19 m; 7.28 s; 7.63 vs(br); 7.91 vs(br); 8.30 vs(br); 8.60 s; 9.44 s; 9.59 s; 9.79 s; 10.26 vs; 10.88 m; 11.06 m; 11.47 m; 11.76 m; 12.52 m; 13.50 m; 13.79 m(sh); and 14.03 s.

(NN-Bistrifluoromethylamino-oxy)cyclopropane carboxylate $\overline{CH_2CH_2}CHCOON(CF_3)_2$ (64) liquid

3.23 w; 3.30 m; 3.42 w; 5.53 m(br); 6.88 m; 7.02 m; 7.25 s; 7.68 vs(br); 7.91 vs(br); 8.30 vs(br); 9.00 m; 9.40 s; 9.59 s; 9.75 s; 10.00 m; 10.30 vs; 11.00 m; 11.26 m; 11.59 m; 12.17 w; 12.44 w; 12.76 m; 13.62 m; and 14.10 s.

Cyclopropyl-(NN-bistrifluoromethylamino-oxy)phenylmethane

$\overline{CH_2CH_2}CHCHPhON(CF_3)_2$ (69) liquid

3.27 m; 3.29 m; 3.33 s; 3.36 s; 3.44 w; 6.23 w; 6.70 w; 6.90 s; 7.0 m; 7.19 m(br); 7.75 vs(br); 8.13 vs(br); 8.40 vs(br); 9.35 m; 9.79 vs(br); 10.53 vs(br); 11.11 s; 11.60 s; 11.76 m; 12.05 w; 12.66 w; 13.50 s; and 14.60 s.

10-(NN-Bistrifluoromethylamino-oxy)-2-pinene

$(CF_3)_2NOCH_2\overline{C:CHCH_2\underline{CHCH_2}CHCMe_2}$ (72) liquid

3.29 w; 3.34 s; 3.40 s(br); 3.42 s; 3.46 s(sh); 3.52 m; 6.04 w; 6.81 m; 6.90 w; 6.98 m; 7.21 m; 7.30 m; 7.76 vs(br); 7.95 vs(br); 8.33 vs(br); 8.86 w; 9.23 w; 10.40 vs; 10.80 w; 10.99 w; 11.30 w; 12.22 w(br); 12.53 m; 12.87 w; 14.25 s; and 15.63 w.

1-(NN-Bistrifluoromethylamino-oxy)methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene

$(CF_3)_2NOCH_2\overline{C:CHCH_2CH[CMe_2ON(CF_3)_2]CH_2CH_2}$ (73) liquid

3.33 m(sh); 3.38 s; 3.45 m(sh); 5.91 w; 6.02 w; 6.78 w; 6.84 m; 6.88 m(sh); 7.18 m; 7.27 s; 7.34 s; 7.69 vs(br); 7.95 vs(br); 8.32 vs(br); 8.98 m; 9.19 m; 9.42 s(sh); 9.62 s; 10.34 s; 10.76 m; 11.14 w; 11.59 w; 11.96 w; 12.41 m; and 14.22 s.

2-Exo-10-bis(NN-bistrifluoromethylamino-oxy)pinane

$(CF_3)_2NOCH_2\overline{CON(CF_3)_2CH_2CH_2CHCH_2CHCMe_2}$ (74a) liquid

3.39 m(sh); 3.43 m; 3.48 m; 6.74 m; 6.80 m; 7.18 m; 7.69 vs; 7.97 vs(br); 8.30 vs(br); 8.90 m; 9.21 m; 9.48 s; 9.57 s(sh); 9.98 w(sh); 10.37 s; 10.73 w; 11.36 w; 11.90 m; 12.05 m(sh); and 14.24 m.

2-Endo-10-bis(NN-bistrifluoromethylamino-oxy)pinane

$(CF_3)_2NOCH_2\overline{CON(CF_3)_2CH_2CH_2CHCH_2CHCMe_2}$ (74b) liquid

3.36 m(sh); 3 41 m(sh); 3.44 m; 3.49 m; 6.76 m(sh); 6.83 m; 6.92 w(sh); 7.20 m; 7.31 m; 7.72 vs(br); 7.96 vs(br); 8.33 vs(br); 8.98 m; 9.18 m; 9.50 s(br); 9.83 m; 10.42 s; 10.70 m(sh); 11.63 w; 12.20 m(br); and 14.29 m.

3-(NN-Bistrifluoromethylamino-oxy)-2(10)-pinene

$CH_2{:}\overline{CCHON(CF_3)_2CH_2CHCH_2CHCMe_2}$ (78) liquid

(mixture of diastereoisomers)

3.25 w; 3.36 s; 3.41 s; 3.48 m; 5.49 w(br); 6.08 m; 6.81 m; 6.88 m; 6.96 m; 7.08 m; 7.22 m; 7.30 m; 7.41 m; 7.70 vs(br); 7.97 vs(br); 8.33 vs(br); 8.73 s; 9.01 m; 9.24 m; 9.35 m; 9.48 m; 9.64 s; 9.76 s; 10.0 w; 10.36 s; 10.60 m; 10.95 s; 11.26 w; 11.45 w; 11.60 m; 11.90 w; 12.18 m; 12.42 w; 12.85 m; 14.08 s; 14.33 m; and 14.51 m.

2,3-Bis(NN-bistrifluoromethylamino-oxy)pinane

$(CF_3)_2NOCMeCHON(CF_3)_2CH_2CHCH_2CHCMe_2$ (79) liquid

(mixture of diastereoisomers)

3.34 s; 3.40 s; 3.47 m; 4.76 w; 6.78 m; 6.85 m(br); 7.16 m; 7.23 m; 7.30 m; 7.72 vs(br); 8.02 vs(br); 8.34 vs(br); 8.98 m; 9.23 s; 9.45 s; 9.60 s; 10.09 m; 10.42 s; 10.75 m; 11.43 w; 11.75 m; 12.21 m; 13.12 w; 13.50 w; and 14.26 s.

A mixture of 10-(NN-bistrifluoromethylamino-oxy)-2-pinene (72) and 10-NN-bistrifluoromethylamino-2-pinene

$(CF_3)_2NCH_2C:CHCH_2CHCH_2CHCMe_2$ (81) liquid

3.29 w(sh); 3.33 m; 3.38 s; 3.42 s; 3.45 m(sh); 3.52 m; 6.05 w; 6.82 m(sh); 6.87 m; 6.99 m; 7.27 vs(br); 7.52 vs(br); 7.72 vs(br); 7.94 vs(br); 8.26 v (br); 8.62 vs(br); 8.85 s(sh); 9.11 m; 9.44 m; 9.62 m; 9.90 vs; 10.34 s; 10.89 m; 11.24 m; 12.12 w; 12.48 w; 12.77 w; 14.06 s; and 14.41 s.

2-Exo-3-endo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene $(CF_3)_2NOCHCHON(CF_3)_2CHCH:CHCHCH_2$ (89) liquid

3.25 w; 3.33 m; 3.38 m; 3.47 w; 4.13 w(br); 4.68 w; 6.10 w; 6.33 w; 6.49 w; 6.86 m; 7.32 m(sh); 7.41 s(sh); 7.70 vs(br); 8.00 vs(br); 8.31 vs(br); 8.89 s; 9.02 m; 9.51 s(sh); 9.61 s; 9.92 m; 10.10 m(sh); 10.35 s; 10.40 s(sh); 10.88 m; 11.07 m; 11.43 w; 11.71 w; 11.90 w; 12.29 m(sh); 12.41 m; 12.90 m; 13.33 w; 13.77 s; 14.08 s; 14.84 m; and 15.60 m.

2-Exo-3-exo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene $(CF_3)_2NOCHCHON(CF_3)_2CHCH:CHCHCH_2$ (90) liquid

3.25 w; 3.32 m; 3.36 m; 3.38 m; 3.47 w; 4.12 w(br); 4.68 w; 5.97 w; 6.12 w; 6.33 w; 6.50 w; 6.59 w; 6.89 m; 7.08 w; 7.38 s; 7.43 s; 7.72 vs(br); 8.00 vs(br); 8.32 vs(br); 8.79 m; 8.94 m; 9.08 m; 9.48 vs; 9.63 s(sh); 9.98 m; 10.14 s; 10.34 s; 10.41 s(sh); 10.64 m; 11.0 m; 11.48 w; 11.85 w; 12.41 m; 12.63 m; 12.84 m; 13.59 s; 13.97 s; 14.10 s; and 15.58 m.

3-(NN-Bistrifluoromethylamino-oxy)cyclo-octa-1,5-diene $(CF_3)_2NOCHCH:CHCH_2CH_2CH:CHCH_2$ (99) liquid
(tentatively identified)

3.33 m; 3.41 m; 3.47 m; 4.19 w; 6.02 m; 6.71 m; 6.97 m; 7.09 m; 7.77 vs(br); 7.98 vs(br); 8.33 vs(br); 9.03 m; 9.29 m; 9.63 s; 9.99 m; 10.10 m; 10.41 s; 12.45 m; 12.77 m; and 14.16 s.

Trans-1-NN-bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)cyclo-oct-5-ene

$(CF_3)_2N\overline{CHCH_2CH_2CH:CHCH_2CH_2}CHON(CF_3)_2$ (103a) liquid

3.29 w; 3.38 m(br); 3.46 w; 5.87 w; 6.07 w; 6.71 w(sh); 6.79 m; 6.85 m; 6.94 m(br); 7.47 vs(br); 7.75 vs(br); 7.96 vs(br); 8.30 vs(br); 8.70 vs(br); 9.21 m; 9.40 m; 9.69 s; 9.82 s; 10.0 s; 10.10 s; 10.26 s; 10.36 vs; 10.49 s; 10.95 w; 11.19 m; 11.38 m; 12.00 w; 12.35 w; 12.50 w; 12.82 w; 13.16 w; 13.29 m; 14.08 vs; 14.22 s; 14.39 m(sh); and 14.77 m.

Cis-1-NN-bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)cyclo-oct-5-ene

$(CF_3)_2N\overline{CHCH_2CH_2CH:CHCH_2CH_2}CHON(CF_3)_2$ (103b) liquid

3.31 m; 3.39 m; 3.45 m(sh); 3.48 m; 3.52 w; 5.87 w(br), 6.05 w; 6.72 m; 6.97 s(br); 7.49 vs(br); 7.75 vs(br); 7.96 vs(br); 8.30 vs(br); 8.70 vs(br); 9.05 s(sh); 9.35 s; 9.62 s; 10.05 s; 10.22 s(sh); 10.33 vs; 10.64 s; 10.92 w; 11.39 m; 11.81 w; 11.92 w; 12.18 m; 12.30 m; 12.52 w; 12.82 w; 12.99 w; 13.50 s; 13.66 s; 14.03 vs; and 14.49 s.

3-(NN-Bistrifluoromethylamino-oxy)cyclo-oct-1-ene

$(CF_3)_2NO\overline{CHCH:CHCH_2CH_2CH_2CH_2CH_2}$ (105) liquid

3.30 m; 3.41 s; 3.50 s; 6.06 w; 6.90 m(br); 7.36 m(sh); 7.58 m(sh); 7.76 vs(br); 8.00 vs(br); 8.33 vs(br); 8.55 s; 8.73 m; 8.95 m; 9.21 w; 9.62 vs; 9.87 m; 10.40 vs; 10.53 m; 10.62 m(sh); 11.24 w; 11.57 w; 11.76 w; 12.36 m; 12.80 m; 13.18 s; 13.21 m(sh); 13.59 m; 13.95 s; and 14.12 vs.

1,2-Bis(NN-bistrifluoromethylamino-oxy)cyclo-octane

$(CF_3)_2NO\overline{CHCH_2CH_2CH_2CH_2CH_2CH_2CH}ON(CF_3)_2$ (106) liquid

3.41 s; 3.50 m; 6.76 m(sh); 6.81 m; 6.96 m; 7.33 m(sh); 7.73 vs(br); 8.01 vs(br); 8.33 vs(br); 8.93 m; 9.60 vs; 10.42 vs; 10.53 m; 11.24 w; 11.47 w; 11.98 w; 12.17 w; 12.44 w; 13.44 w; and 14.12 vs.

3-(NN-Bistrifluoromethylamino-oxy)-3-phenylpropene

$(CF_3)_2NOCHPhCH:CH_2$ (109) liquid

3.24 w; 3.26 w; 3.29 w; 3.34 w; 3.42 w(br); 5.13 w(br); 5.32 w; 6.10 w; 6.24 w; 6.70 w; 6.89 m; 7.03 m; 7.06 w(sh); 7.41 m(sh); 7.71 vs(br); 7.97 vs(br); 8.33 vs(br); 8.73 m; 9.09 w; 9.31 w; 9.64 m; 9.98 m(sh); 10.17 s; 10.40 vs; 10.66 s; 10.88 m; 11.0 m; 11.53 w; 11.90 w; 12.45 w; 13.12 m; 13.33 m; 14.10 vs; 14.33 vs; and 14.53 m.

Trans-3-(NN-bistrifluoromethylamino-oxy)-1-phenylpropene

$(CF_3)_2NOCH_2CH:CHPh$ (110) liquid

3.24 w; 3.27 w; 3.29 w; 3.39 w; 3.45 w; 6.04 m(br); 6.26 w; 6.34 w; 6.69 m; 6.82 w; 6.90 m; 7.30 m; 7.72 vs(br); 7.94 vs(br); 8.30 vs(br); 8.56 s(sh); 8.97 m; 9.10 w(sh); 9.35 m; 9.62 s; 10.0 m(sh); 10.18 m(sh); 10.34 vs; 10.71 w; 10.96 w(sh); 11.96 w; 12.38 w; 12.58 w; 13.36 s; 14.08 s; and 14.45 s.

1,2,3-Tri(NN-bistrifluoromethylamino-oxy)-3-phenylpropane

$(CF_3)_2NOCH_2CHON(CF_3)_2CHPhON(CF_3)_2$ (111) liquid

3.26 w; 3.29 w; 3.37 w; 6.22 w; 6.69 w; 6.77 w; 6.86 w; 7.30 m(sh); 7.69 vs(br); 7.97 vs(br); 8.27 vs(br); 9.01 m; 9.26 m(sh); 9.57 s; 10.40 vs; 12.35 m; 12.58 w(sh); 13.04 m; 13.42 m; 14.08 s; and 14.29 m.

1,2,5-Tri(NN-bistrifluoromethylamino-oxy)pent-3-ene

$(CF_3)_2NOCH_2CHON(CF_3)_2CH:CHCH_2ON(CF_3)_2$ (115) liquid

3.31 w(sh); 3.34 w(sh); 3.39 m; 3.47 w; 4.12 w(br); 4.68 w; 5.89 w; 5.98 w; 6.24 w; 6.50 w; 6.78 w; 6.86 m; 6.93 w; 7.08 w; 7.27 s; 7.72 vs(br); 7.97 vs(br); 8.33 vs(br); 9.01 m; 9.40 s; 9.57 s; 10.0 m; 10.37 s; 11.44 w(br); 12.36 m; 13.51 w; and 14.10 vs.

1-NN-Bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)-3-phenylpropane

$(CF_3)_2NCH_2CHON(CF_3)_2CH_2Ph$ (121) liquid

3.22 w(sh); 3.24 w; 3.25 w; 3.29 m; 3.32 w; 3.36 w; 3.40 w; 3.48 w; 6.22 w; 6.30 w; 6.68 m; 6.90 m; 7.22 vs; 7.52 vs(br); 7.68 vs(br); 7.97 vs(br); 8.23 vs(br); 8.58 vs(br); 9.01 vs(br); 9.52 s; 10.34 vs; 10.50 vs; 10.91 m; 11.43 w; 11.88 w; 12.25 w; 13.30 s; 14.04 vs; and 14.25 vs.

1-NN-Bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)pent-4-ene

$(CF_3)_2NCH_2CHON(CF_3)_2CH_2CH{:}CH_2$ (122) liquid

3.24 m; 3.31 w(sh); 3.35 m; 3.39 w(sh); 3.42 w; 4.13 w; 4.67 w; 5.39 w(br); 5.87 w(br); 6.09 m; 6.49 w(br); 6.58 w; 6.93 m(sh); 6.99 m(sh); 7.04 m; 7.25 vs; 7.43 vs(br); 7.55 vs(br); 7.69 vs(br); 8.00 vs(br); 8.29 vs(br); 8.57 vs(br); 9.09 s(br); 9.54 s(br) 10.08 s; 10.37 vs; 10.53 s; 10.75 s; 11.40 w; 11.88 m; 12.27 m; 12.52 w(sh); 13.46 m; 14.08 vs; and 14.33 s.

APPENDIX B

N.M.R. SPECTRA

The ^{1}H n.m.r. spectra are recorded in p.p.m. relative to an external T.M.S. reference at 0.0 p.p.m., except where stated. The ^{19}F n.m.r. spectra are recorded in p.p.m. relative to an external $CF_3SCH_2CHBrCH_2Br$ reference, except where stated.

(s= singlet, d= doublet, t= triplet, q= quartet, c= complex, m= multiplet, b= broad).

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(CF_3)_2NOCH_bH_c$ (d) / $(CF_3)_2NOCMe$ (e) (a) / $(CF_3)_2NOCH_bH_c$ (d) (9)	^1H*	a.-6.0	s	3
		b.-3.25	AB	2
		c.-3.15	AB	2
		$J_{b,c}$=11Hz		
	^{19}F**	d. -7.5	s	2
		e. -9.5	bs	1
$(CF_3)_2NOCH_2CMe_2Br$ (c) (b) (a) (10)	^1H*	a.-5.7	s	3
		b.-3.8	s	1
	^{19}F**	c. -11.3	s	-
$(CF_3)_2NOCMeCH_bH_cBr$ (f) (a) / $(CF_3)_2NOCH_2$ (e) (d) (11)	^1H	a. 1.35	s	3
		b. 3.27	AB	1
		c. 3.43	AB	1
		d. 4.14	s	2
		$J_{b,c}$=11Hz		
	^{19}F***	e. 42.4	s	1
		f. 40.6	s	1

* Spectrum obtained using p-$C_6H_4Cl_2$ reference.
** Spectrum obtained using T.F.A. reference.
*** Spectrum obtained using p-$CF_2ClSC_6H_4Cl/CCl_4$ reference.

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(CF_3)_2NOCMeCH_bH_cCl$ (f, a) $(CF_3)_2NOCH_2$ (e, d) (17)	^1H	a. 1.22 b. 3.32 c. 3.44 d. 4.03 $J_{b,c}$=12Hz	s AB AB s	3 1 1 2
	^{19}F*	e. 42.65 f. 40.8	s s	1 1
CF_3 (f), CF_3 (e) $NOCMeCl$ (a) $(CF_3)_2NOCH_bH_c$ (d) (18)	^1H	a. 1.68 b. 3.96 c. 4.14 $J_{b,c}$=10Hz	s AB AB	3 1 1
	^{19}F	d. 30.1 e. 27.55 f. 26.9 $J_{e,f}$=11Hz	s q q	2 1 1
$(CF_3)_2NOCH_2CMeCl_2$ (c, b, a)** (19)	^1H	a. 1.91 b. 4.12	s s	3 2
	^{19}F	c. 29.1	s	-

* Spectrum obtained using p-$CF_2ClSC_6H_4Cl/CCl_4$ reference.

** Spectrum obtained from a mixture of the compound with 2,2-dichloropropane.

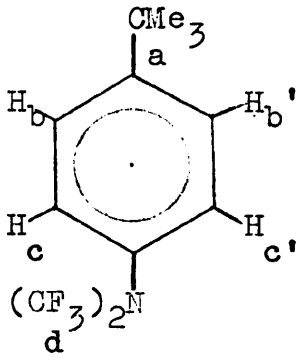
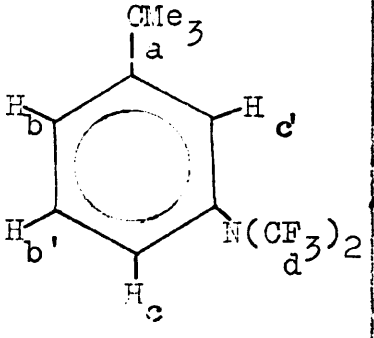
Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(CF_3)_2NOCH_bH_c$ $\vert$ $(CF_3)_2NOCPhMe$ (20)	^1H	a. 1.46 b. 3.75 c. 4.01 d. 6.94 $J_{b,c}$=10Hz	s AB AB m	3 1 1 5
	^{19}F	e. 29.65 f. 27.4	s c	1 1
$(CF_3)_2NOCHCCl_3$ $\vert$ $(CF_3)_2NOCH_2$ (22)	^1H*	a. ca.4.7	c	-
	^{19}F	b. 28.15 c. 26.7	s bs	1 1
$(CF_3)_2NOCCl_2CHCl$ $\vert$ $(CF_3)_2NOCH_aH_b$ (23)	^1H	a,b. 4.3 c. 4.68 $J_{a,c}$=9Hz $J_{b,c}$=2Hz	c dd	2 1
	^{19}F	d. 29.5 e. 25.4	s s	1 1

* Spectrum obtained using internal T.M.S. reference in CCl_4.

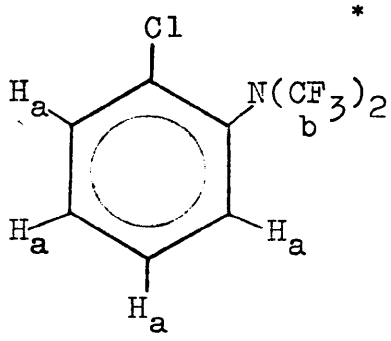
Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(CF_3)_2NOCH_bH_c$ * $(CF_3)_2NOCMeCCl_3$ (24)	^1H	a. 1.74 b. 4.33 c. 4.47 $J_{b,c}$=11Hz	s AB AB	3 1 1
	^{19}F	d. 29.4 e. 26.6	s c	1 1
$(CF_3)_2NOCCl_2CMeCl_2$ * $(CF_3)_2NOCH_bH_c$ (25)	^1H	a. 1.82 b. 4.54 c. 4.62 $J_{b,c}$=11Hz	s AB AB	3 1 1
	^{19}F	d. 29.4 e. 24.9	s s	1 1
$(CF_3)_2NOCMeCH_2Cl$ $(CF_3)_2NOCCl_2$ (26)	^1H	a. 1.75 b. 3.96	s s	3 2
	^{19}F	c. 26.65 d. 24.9	s s	1 1

* Spectrum obtained from a mixture of the two compounds.

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(\underset{d}{CF_3})_2NOCCl_2CH_cCl$ | $(\underset{e}{CF_3})_2NCH_aH_b$ (29)	^1H	a. 3.58 b. 4.05 c. 4.37 $\underline{J}_{a,b}$=16Hz $\underline{J}_{a,c}$=10Hz $\underline{J}_{b,c}$=2Hz	ABd ABd dd	1 1 1
	^{19}F	d. 25.4 e. 18.6	s s	1 1
$(\underset{c}{CF_3})_2NOCCl_2CMeCl$ | a $(\underset{d}{CF_3})_2NCH_{2}$ (b) (30)	^1H	a. 1.81 b. 3.93	s bs	3 2
	^{19}F	c. 24.8 d. 17.1	s s	1 1
$(\underset{c}{CF_3})_2NOCCl_2CMeCl$ | a CH_2Cl (b) (31)	^1H	a. 2.02 b. 4.10	s s	3 2
	^{19}F	c. 24.1	s	-

Compound	Nucleus	Chem.shift (p.p.m.)	Multiplicity	Relative intensity
$(CF_3)_2NOCH_2CPhMe_2$ (d, b, c, a) (39)	^1H	a. 0.95 b. 3.63 c. 6.78	s s m	6 2 5
	^{19}F*	d. 41.65	s	-
 (40)	^1H	a. 0.83 b. ca. 6.9 c.	s AA'BB'	9 4
	^{19}F	d. 16.0	s	-
 (41)	^1H	a. 0.83 b. 6.74 c. 7.0	s c c	9 2 2
	^{19}F	d. 16.0	s	-

* Spectrum obtained using p-$CF_2ClSC_6H_4Cl/CCl_4$ reference.

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(CF_3)_2NOCH_2CPh_2Me$ (42)	^1H	a. 1.35 b. 4.0 c. 6.62	s s s	3 2 10
	^{19}F**	d. -10.0	s	-
 (52) *	^1H	a. 6.9	bs	-
	^{19}F	b. 16.75	s	-
$(CF_3)_2NOCOCMe_2OCOMe$ (59)	^1H	a. 1.29 b. 1.69	s s	2 1
	^{19}F	c. 28.35	s	-

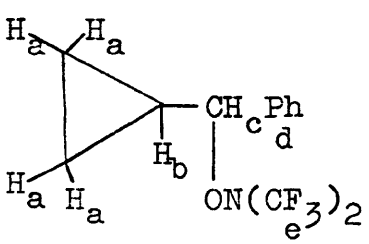
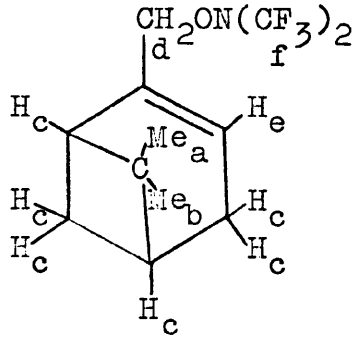
* Spectrum obtained from a mixture of the compound with a minor unidentified component.

** Spectrum obtained using T.F.A. reference.

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
$(CF_3)_2NOCH_2CMe_2$ (c, a) OCOMe (b) * (60)	^1H	a. 1.13	s	6
		b. 1.55	s	3
		c. 3.96	s	2
	^{19}F	d. 29.7	s	-
$[(CF_3)_2NO]_2CHCMe_2$ (d; c, a) OCOMe (b) * (61)	^1H	a. 1.18	s	6
		b. 1.55	s	3
		c. 5.21	s	1
	^{19}F	d. 28.8	bs	-
H_a, H_a, C=O, H_b, $ON(CF_3)_2$ (c), H_a, H_a (64)	^1H**	a.-6.41	d	4
		b.-5.76	m	1
		$J_{a,b}$=6Hz		
	^{19}F	c. 29.05	s	-

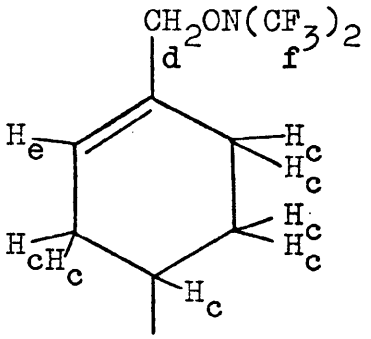
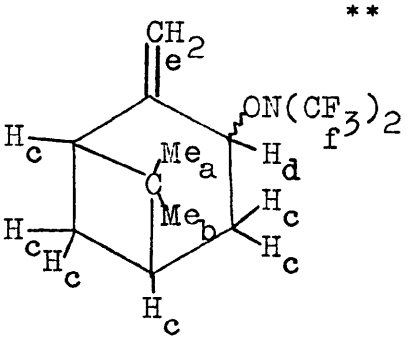
* Spectra obtained from a mixture of the two compounds (ratio ca. 3:1)

** Values obtained are relative to p-$Cl_2C_6H_4$ reference.

Compound	Nucleus	Chem.shift (p.p.m.)	Multiplicity	Relative intensity
 (69)	^1H	a. ca. -8.2 *	c	4
		b. -7.3 *	c	1
		c. -4.55 *	d	1
		d. 6.87	m	5
		$J_{b,c}$=9Hz		
	^{19}F	e. 27.75	bs	-
 (72)	^1H	a. 0.62	s	3
		b. 1.08	s	3
		c. 1.4-2.3	c	6
		d. 4.11	s	2
		e. 5.37	m	1
	^{19}F**	f. 41.73	s	-

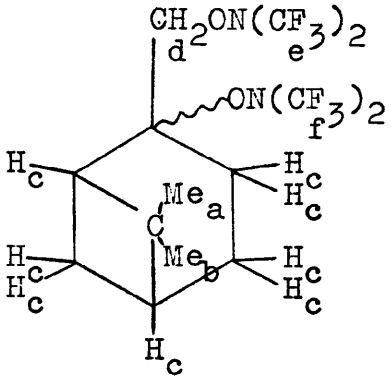
* Values obtained are relative to p-$Cl_2C_6H_4$ reference.

** Spectrum obtained using p-$CF_2ClSC_6H_4$/CCl_4 reference.

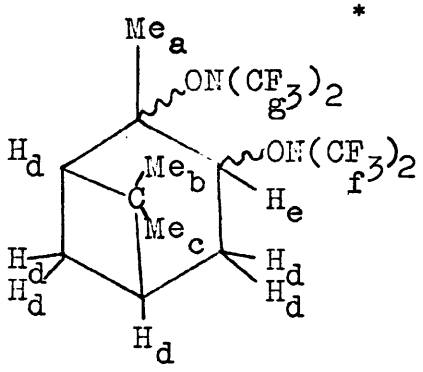
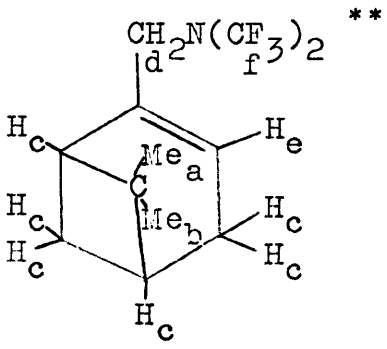
Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 (73)	^1H	a. 0.63	s	3
		b. 1.15	bs	3
		c. 1.4-2.4	c	7
		d. 4.20	s	2
		e. 5.50	m	1
	^{19}F*	f. 42.2	s	1
		g. 41.1	bs	1
 ** (78)	^1H	a. 0.44	s	6
		b. 1.07	s	6
		c. 1.4-2.3	c	12
		d. 4.31	m	1
		4.37	m	1
		e. 4.75	s	2
		4.88	s	2
	^{19}F	f. 27.8	c	1
		26.6	c	1

* Spectrum obtained using p-$CF_2ClSC_6H_4Cl/CCl_4$ reference.

** Spectrum obtained from a mixture of two diastereoisomers (ratio 1:1).

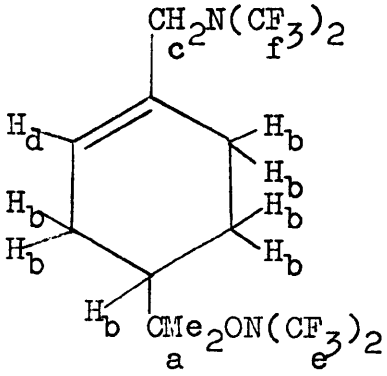
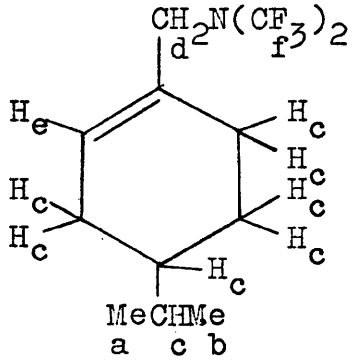
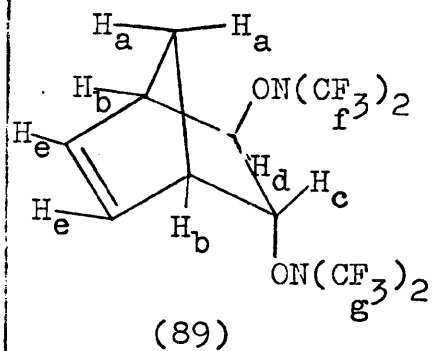
Compound	Nucleus	Chem.shift (p.p.m.)	Multiplicity	Relative intensity
 (74)	^1H	Diastereoisomer 1		
		a. 0.91	s	3
		b. 1.05	s	3
		c. 1.2-2.4	c	8
		d. 4.09	m	2
	^1H	Diastereoisomer 2		
		a. 0.84	s	3
		b. 1.13	s	3
		c. 1.2-2.3	c	8
		d. 4.05	m	2
	^{19}F*	Diastereoisomer 1		
		e. 42.2	s	1
		f. 40.5	c	1
	^{19}F	Diastereoisomer 2		
		e. 28.9	bs	1
		f. 27.0	c	1

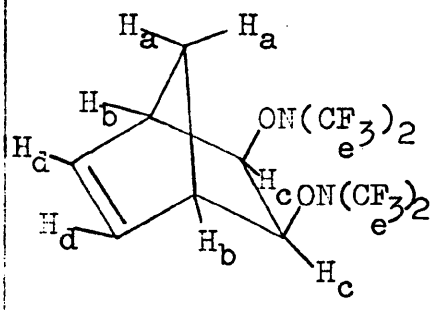
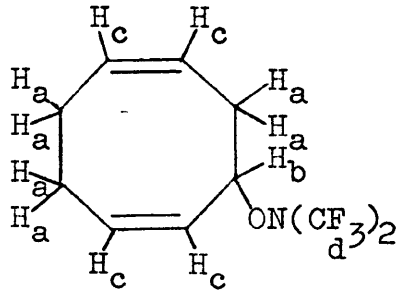
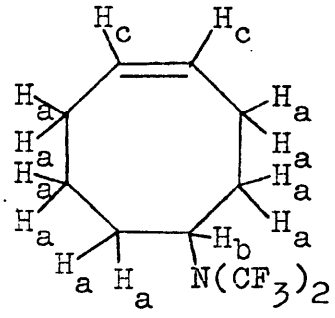
* Spectrum obtained using p-$CF_2ClSC_6H_4Cl/CCl_4$ reference.

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 * (79)	^{1}H	a. 0.86	s	3
		b. 1.18	s	3
		c. 1.38	s	3
		d. 1.5-2.5	c	7
		e. 4.56	m	1
	^{19}F	f. 27.8	c	1
		g. 26.9 to 27.1	c	1
 ** (81)	^{1}H	a. 0.61	s	3
		b. 1.06	s	3
		c. 1.4-2.4	c	6
		d. 3.37	bs	2
		e. 5.23	m	1
	^{19}F	f. 18.15	s	-

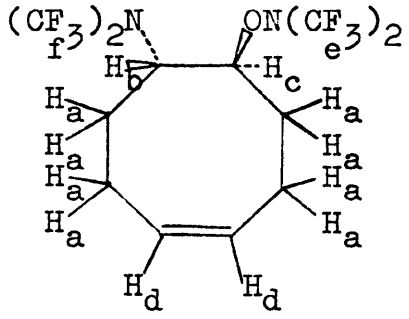
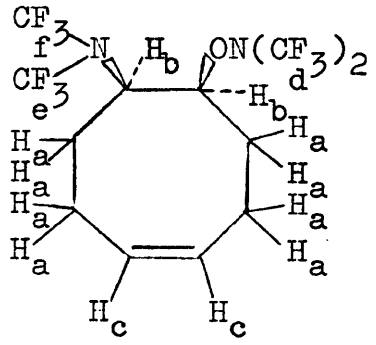
* Mixture of diastereoisomers

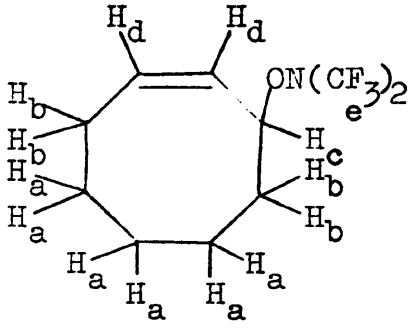
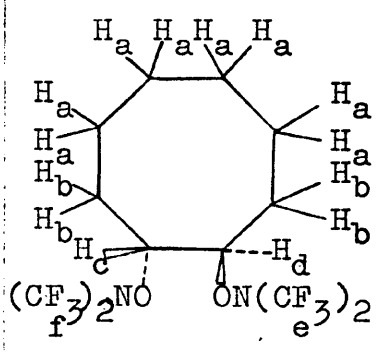
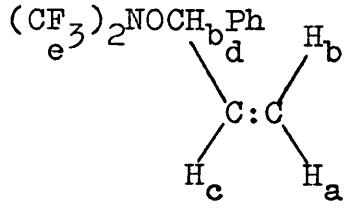
**Spectrum obtained from a mixture of the compound with 10-(NN-bistrifluoromethylamino-oxy)-2-pinene (72).

Compound	Nucleus	Chem.shift (p.p.m.)	Multiplicity	Relative intensity
 (82)	^1H	a. 1.04	s	6
		b. 1.3-2.1	c	7
		c. 3.44	bs	2
		d. 5.43	m	1
	^{19}F	e. 26.6	s	1
		f. 18.4	s	1
 (83)	^1H	a. 0.64	s	3
		b. 0.70	s	3
		c. 0.9-2.0	c	8
		d. 3.40	bs	2
		e. 5.39	m	1
	^{19}F	f. 18.4	s	-
 (89)	^1H	a. 1.54	s	2
		b. 2.79	c	2
		c. 3.85	s	1
		d. 4.37	bs	1
		e. 5.91	m	2
	^{19}F	f. 29.2	s	1
		g. 29.0	bs	1

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 (90)	^1H	a. 1.70	m	2
		b. 2.90	bs	2
		c. 4.02	s	2
		d. 5.86	m	2
	^{19}F	e. 28.85	c	-
 (99)	^1H	a. 1.7-2.6	c	6
		b. 4.8	m	1
		c. 5.3	c	4
	^{19}F	d. 28.5	s	-
 (102)	^1H	a. 1.2-2.6	c	-
		b. 3.1-3.7	c	-
		c. ca. 5.7	c	-
	^{19}F	d. 14.15	s	-

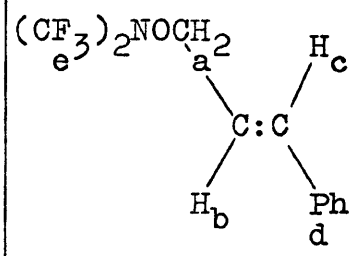
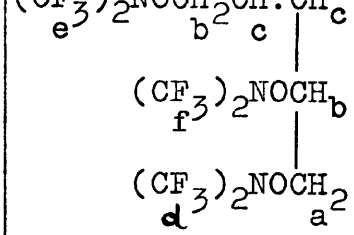
* Spectrum obtained in carbon tetrachloride solution (15%); sample contaminated with several minor components.

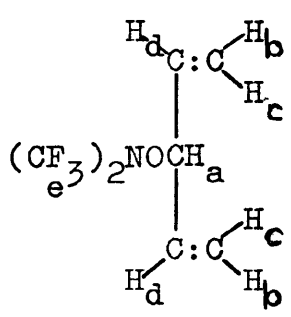
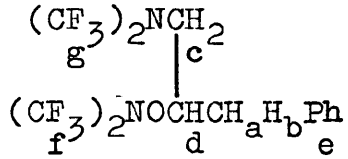
Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 (103a)	^1H	a. 1.2-2.5	c	8
		b. ca. 4.0	c	1
		c. ca. 4.25	c	1
		d. ca. 5.5	c	2
	^{19}F	e. 27.9	c	6
		d. 15.7	s	6
 (103b)	^1H	a. 1.3-2.5	c	8
		b. 3.6-4.3	c	2
		c. ca. 5.4	c	2
	^{19}F	d. 28.0	bs	6
		e. 11.9	c	3
		f. 18.7	c	3

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 (105)	^1H	a. 1.35	c	6
		b. 1.89	c	4
		c. 4.73	c	1
		d. 5.39	m	2
	^{19}F	e. 28.4	c	-
 (106)	^1H	a. 1.39	c	8
		b. 1.75	c	4
		c. 4.06	c	1
		d. 4.18	c	1
	^{19}F	e. 28.55	s	1
		f. 28.25	bs	1
 (109)	^1H	a. 4.60	c	1
		b. 4.75	c	2
		c. 5.49	m	1
		d. 6.66	c	5
	^{19}F	e. 28.0	c	-

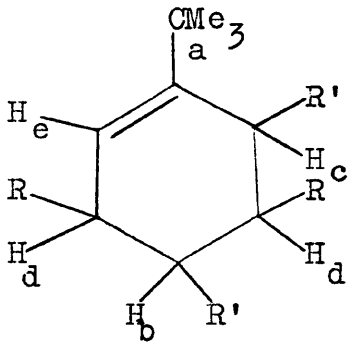
Compound	Nucleus	Chem.shift (p.p.m.)	Multiplicity	Relative intensity
$(CF_3)_2NOCH_aH_b$ (f) $(CF_3)_2NOCH_c$ (g) $(CF_3)_2NOCH_dPh_e$ (h) (111)	^1H	Diastereoisomer 1		
		a,b. 3.95	ABd	2
		c. 4.46	c	1
		d. 4.89	c	1
		e. 6.95	bs	5
	^1H*	Diastereoisomer 2		
		a. 3.60	ABc	1
		b. 3.99	ABc	1
		c. 4.34	c	1
		d. 4.85	d	1
		e. 6.97	bs	5
		$J_{c,d}$=7Hz		
	^{19}F	Diastereoisomer 1		
		f. 30.01	s	6
		g. 28.95	s	6
		h. 28.85	bs	6
	^{19}F*	Diastereoisomer 2		
		f. 29.7	bs	6
		g. 28.65	bs	12

* Spectrum obtained in carbon tetrachloride solution (15%).

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 (110)	^1H	a. 3.92 b. 5.44 c. 5.80 d. 6.58 $J_{a,b}$=7Hz $J_{b,c}$=15Hz	d ABt AB bs	2 1 1 5
	^{19}F	e. 29.0	s	-
 (115)	^1H	a. 3.84 b. 4.19 c. 5.51 $J_{a,b}$=5Hz	d c m	2 3 2
	^{19}F	d. 30.15 e. 29.9 f. 29.2	s s c	1 1 1

Compound	Nucleus	Chem.shift (p.p.m.)	Multi-plicity	Relative intensity
 * (116)	^1H	a. 4.33 b. 4.78 c. 4.92 d. 5.37 $J_{a,d}$=7Hz	t c m m	1 2 2 2
	^{19}F	e. 29.0	s	-
 (121)	^1H	a. 2.24 b. 2.76 c. 2.86 d. 3.99 e. 6.77 $J_{a,b}$=14Hz $J_{a,d}$=8Hz $J_{b,d}$=6Hz	ABd ABd c c c	1 1 2 1 5
	^{19}F	f. 28.45 g. 18.85	bs s	1 1

* Spectrum obtained from a mixture of the compound with NN-bistrifluoromethylhydroxylamine (ratio ca. 1:1).

Compound	Nucleus	Chem.shift (p.p.m.)	Multiplicity	Relative intensity
$(CF_3)_2NCH_2$ (h, b) / $(CF_3)_2NOCH_c$ (g) / $CH_2CH{:}CH_dH_e$ (a, f) (122)	^1H	a. 2.10	c	2
		b. 2.99	m	2
		c. 3.87	c	1
		d. 4.71	bs	1
		e. 4.84	s	1
		f. 5.33	m	1
		$J_{d,f}$=6Hz		
	^{19}F	g. 28.95	bs	1
		h. 19.3	s	1
 *	^1H	a. 0.97	s	9
		b. 3.1-3.9	c	1
		c. 4.2-4.6	c	1
		d. 4.6-5.2	c	2
		e. 5.7-6.4	c	1
	^{19}F	27.5-28.5, 20.1, 16.3-17.7, 11.2-11.9.		

*Spectrum obtained from a mixture of isomers [where R= $(CF_3)_2NO$; R'=$(CF_3)_2N$].

APPENDIX C

MASS SPECTRA

In the mass spectral tables presented in Appendix C, isotopic ions have been grouped together and the relative abundance of each ion has been corrected for the presence of isotopes.

The intensities of isotope peaks of ions containing chlorine atoms are dependent on the number of chlorine atoms present in the ion, i.e.

Number of chlorine atoms	% P + 2	% P + 4	% relative to P (100%) P + 6
1	32.6		
2	65.3	10.6	
3	99.8	31.9	3.47

and use has been made of isotopic distributions in assigning structures to ions.

1,2,3-Tri(NN-bistrifluoromethylamino-oxy)-2-methylpropane

$[(CF_3)_2NOCH_2]_2CMeON(CF_3)_2$ (9) $C_{10}H_7F_{18}N_3O_3$ (M, 559)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
391	$C_8H_7F_{12}N_2O_2$	1.5	133	C_2F_5N	1.9
377	$C_7H_5F_{12}N_2O_2$	4.8	69	CF_3	32.8
223	$C_6H_7F_6NO$	0.7	58	C_3H_6O	21.6
222	$C_6H_6F_6NO$	2.0	57	C_3H_5O	25.0
209	$C_5H_5F_6NO$	1.9	55	C_4H_7/C_3H_3O	15.6
182	$C_3H_2F_6NO$	12.1	43	C_2H_3O	100.0
166	$C_3H_2F_6N$	11.7	41	C_3H_5	32.6
150	C_2HF_5NO	13.8	28	C_2H_4	16.5

1-(NN-Bistrifluoromethylamino-oxy)-2-bromo-2-methylpropane

$(CF_3)_2NOCH_2CMe_2Br$ (10) $C_6H_8BrF_6NO$ (M, 303,305)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
303,305	M	33.7	57	C_3H_5O	40.2
288,290	$C_5H_5BrF_6NO$	4.7	55	C_4H_7/C_3H_3O	26.0
222	$C_6H_6F_6NO$	3.6	44	C_2H_4O/CO_2	46.4
182	$C_3H_2F_6NO$	4.1	43	C_2H_3O	100.0
150	C_2HF_5NO	19.7	42	C_3H_6/C_2H_2O	27.2
135,137	C_4H_8Br	1.8	41	C_3H_5	33.3
133	C_2F_5N	3.6	40	C_3H_4	13.9
121,123	C_3H_6Br	7.1	39	C_3H_3	13.4
69	CF_3	38.9	29	C_2H_5	26.7

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane $(CF_3)_2NOCMe(CH_2Br)ON(CF_3)_2$ (11) $C_8H_7BrF_{12}N_2O_2$ (M, 470,472)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
377	$C_7H_5F_{12}N_2O_2$	3.9	57	C_3H_5O	44.1
302,304	$C_6H_7BrF_6NO$	43.0	55	C_4H_7	29.1
288,290	$C_5H_5BrF_6NO$	9.7	44	CO_2/C_2H_4O	15.7
182	$C_3H_2F_6NO$	3.1	43	C_2H_3O	100.0
150	C_2HF_5NO	22.5	42	C_2H_2O/C_3H_6	26.7
93,95	CH_2Br	3.9	41	C_3H_5	35.7
71	-	20.5	39	C_3H_3	13.4
69	CF_3	28.1	29	C_2H_5	24.7

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3-chloro-2-methylpropane $(CF_3)_2NOCH_2CMe(CH_2Cl)ON(CF_3)_2$ (17) $C_8H_7ClF_{12}N_2O_2$ (M,426,428)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
411,413	$C_7H_4ClF_{12}N_2O_2$	0.2	57	C_3H_5O	50.6
377	$C_7H_5F_{12}N_2O_2$	9.2	55	C_4H_7/C_3H_3O	14.1
258,260	$C_6H_7ClF_6NO$	12.0	49,51	CH_2Cl	13.7
244,246	$C_5H_5ClF_6NO$	16.3	44	C_2H_4O	20.4
182	$C_3H_2F_6NO$	15.8	43	C_2H_3O/C_3H_7	100.0
166	$C_3H_2F_6N$	11.0	42	C_3H_6	37.5
150	C_2HF_5NO	27.8	41	C_3H_5	51.5
77,79	C_3H_6Cl	10.7	39	C_3H_3	16.2
69	CF_3	65.6	29	-	36.5

1,2-Bis(NN-bistrifluoromethylamino-oxy)-2-chloropropane

$(CF_3)_2NOCH_2CMeClON(CF_3)_2$ (18) $C_7H_5ClF_{12}N_2O_2$ (M, 412,414)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
377	$C_7H_5F_{12}N_2O_2$	1.2	92,94	C_3H_5ClO	10.2
244,246	$C_5H_5ClF_6NO$	19.7	76,78	C_3H_5Cl	7.1
230,232	$C_4H_3ClF_5NO$	6.1	75,77	C_3H_4Cl	2.0
209	$C_5H_5F_6NO$	1.1	69	CF_3	32.0
182	$C_3H_2F_6NO$	1.3	43	C_2H_3O	100.0
166	$C_3H_2F_6N$	5.1	41	C_3H_5	16.0
150	C_2HF_5NO	12.2	28	C_2H_4	85.2
135	-	16.7			

1-(NN-bistrifluoromethylamino-oxy)-2,2-dichloropropane

$(CF_3)_2NOCH_2CMeCl_2$ (19) $C_5H_5Cl_2F_6NO$ (M, 279,281,283)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
263,265	$C_4HCl_2F_6NO$	0.7	76,78	C_3H_5Cl	10.6
243,245	$C_5H_4ClF_6NO$	7.0	75,77	C_3H_4Cl	70.8
182	$C_3H_2F_6NO$	0.5	69	CF_3	90.7
150	C_2HF_5NO	12.5	61,63	C_2H_2Cl	56.3
133	C_2F_5N	6.4	49,51	CH_2Cl	17.3
111,113,			44	CO_2/C_2H_4O	36.4
115	$C_3H_5Cl_2$	77.2	43	C_2H_3O	25.2
97,99,			41	C_3H_5	13.1
101	$C_2H_3Cl_2$	100.0	39	C_3H_3	26.0

1,2-Bis(NN-bistrifluoromethylamino-oxy)-2-phenylpropane

$(CF_3)_2NOCH_2CPhMeON(CF_3)_2$ (20) $C_{13}H_{10}F_{12}N_2O_2$ (M, 454)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
286	$C_{11}H_{10}F_6NO$	43.0	115	C_9H_7	8.7
272	$C_{10}H_8F_6NO$	10.4	105	C_8H_9	71.8
169	C_2HF_6NO	1.0	103	C_8H_7	17.8
150	C_2HF_5NO	4.1	92	C_7H_8	23.4
134	$C_9H_{10}O$	73.9	77	C_6H_5	22.0
133	C_9H_9O/C_2F_5N	4.4	69	CF_3	37.4
118	C_9H_{10}	100.0	43	C_3H_7/C_2H_3O	55.2
117	C_9H_9				

1-NN-Bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloropropane $(CF_3)_2NCH_2CHClCCl_2ON(CF_3)_2$

$C_7H_3Cl_3F_{12}N_2O$ (29) (M, 464,466,468,470)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
263,265			144,146		
267	$C_4HCl_2F_6NO$	14.3	148	$C_3H_3Cl_3$	1.0
250,252			130,132		
254	$C_3Cl_2F_6NO$	3.6	134	C_2HCl_3	1.8
226,228	$C_5H_3ClF_6N$	1.4	109,111		
214,216	$C_4H_3ClF_6N$	1.8	113	$C_3H_3Cl_2$	3.1
182	$C_3H_2F_6NO$	12.7	78,80	C_2H_3ClO	38.8
166	$C_3H_2F_6N$	100.0	69	CF_3	51.7

1,2-Bis(NN-bistrifluoromethylamino-oxy)-3,3,3-trichloro-propane $(CF_3)_2NOCH_2CH(CCl_3)ON(CF_3)_2$ (22)

$C_7H_3Cl_3F_{12}N_2O_2$ (M, 480, 482, 484, 486)

m/e	Assignment (R^+)	% Int. base
363	$C_6H_3F_{12}N_2O_2$	7.0
312,314,316	$C_5H_3Cl_3F_6NO$	0.5
276,278,280	$C_5H_2Cl_2F_6NO$	2.6
216,218	C_3HClF_6NO	14.9
195	$C_4H_3F_6NO$	1.1
182	$C_3H_2F_6NO$	100.0
168	C_2F_6NO	7.0
144,146,148,150	$C_3H_3Cl_3$	13.0
131,133,135,137	$C_2H_2Cl_3$	31.1
130,132,134	C_2HCl_3	17.8
117,119,121,123	CCl_3	8.3
109,111,113	$C_3H_3Cl_2$	55.0
95,97,99	C_2HCl_2	30.7
83,85,87	$CHCl_2$	18.2
69	CF_3	72.8
63,65	-	14.2

1,3-Bis(NN-bistrifluoromethylamino-oxy)-2,3,3-trichloro-propane $(CF_3)_2NOCH_2CHClCCl_2ON(CF_3)_2$ (23)

$C_7H_3Cl_3F_{12}N_2O_2$ (M, 480, 482, 484, 486)

m/e	Assignment (R^+)	% Int. base
445,447	$C_7H_3Cl_2F_{12}N_2O_2$	1.0
409,411	$C_7H_2ClF_{12}N_2O_2$	1.9
312,314,316,318	$C_5H_3Cl_3F_6NO$	39.4
276,278	$C_5H_2Cl_2F_6NO$	4.0
250,252,254	$C_3Cl_2F_6NO$	18.9
230,232	$C_4H_3ClF_6NO$	3.9
216,218	C_3HClF_6NO	17.3
182	$C_3H_2F_6NO$	57.9
168	C_2F_6NO	12.4
150	C_2HF_5NO	16.3
144,146,148,150	$C_3H_3Cl_3$	19.8
131,133,135,137	$C_2H_2Cl_3$	20.1
130,132,134	C_2HCl_3	12.5
125,127,129	$C_3H_3Cl_2O$	29.8
95,97,99	C_2HCl_2	53.3
83,85,87	$CHCl_2$	31.1
77,79	C_2H_2ClO	15.3
69	CF_3	100.0
63,65,67	CClO	35.3

ca. 2:1 Mixture of 1,2-bis(NN-bistrifluoromethylamino-oxy)-2-methyl-3,3,3-trichloropropane $(CF_3)_2NOCH_2CMe(CCl_3)ON(CF_3)_2$ (24), and 1,3-bis(NN-bistrifluoromethylamino-oxy)-2-methyl-2,3,3-trichloropropane $(CF_3)_2NOCH_2CMeClCCl_2ON(CF_3)_2$ (25), $C_8H_5Cl_3F_{12}N_2O_2$ (M, 494, 496, 498, 500)

m/e	Assignment (R^+)	% Int. base
459,461,463	$C_8H_5Cl_2F_{12}N_2O_2$	8.9
377	$C_7H_5F_{12}N_2O_2$	5.2
326,328,330,332	$C_6H_5Cl_3F_6NO$	26.3
312,314,316	$C_5H_3Cl_3F_6NO$	10.3
291,293,295	$C_6H_5Cl_2F_6NO$	2.3
290,292,294	$C_6H_4Cl_2F_6NO$	37.4
250,252	$C_3Cl_2F_6NO$	1.9
244,246	$C_5H_5ClF_6NO$	5.9
216,218	C_3HClF_6NO	99.1
209	$C_5H_5F_6NO$	1.3
182	$C_3H_2F_6NO$	85.0
158,160,162,164	$C_4H_5Cl_3$	35.2
144,146,148,150	$C_3H_3Cl_3$	27.6
123,125,127	$C_4H_5Cl_2$	50.0
117,119,121,123	CCl_3	11.2
109,111,113	$C_3H_3Cl_2$	25.9
69	CF_3	78.9
43	C_2H_3O	100.0

1,2-Bis(NN-bistrifluoromethylamino-oxy)-2-methyl-1,1,3-trichloropropane $(CF_3)_2NOCCl_2CMe(CH_2Cl)ON(CF_3)_2$ (26)
(tentatively identified) $C_8H_5Cl_3F_{12}N_2O_2$ (M, 494,496,498,500)

m/e	Assignment (R^+)	% Int. base
459,461	$C_8H_5Cl_2F_{12}N_2O_2$	0.3
458,460,462	$C_8H_4Cl_2F_{12}N_2O_2$	4.6
445,447	$C_7H_3Cl_2F_{12}N_2O_2$	0.4
444,446,448	$C_7H_2Cl_2F_{12}N_2O_2$	6.8
326,328,330,332	$C_6H_5Cl_3F_6NO$	30.1
307,309,311	$C_6H_5Cl_3F_5NO/C_6H_5Cl_2F_6NO_2$	3.0
291,293,295	$C_6H_5Cl_2F_6NO$	8.9
290,292,294	$C_6H_4Cl_2F_6NO$	2.7
277,279,281	$C_5H_3Cl_2F_6NO$	7.0
250,252	$C_3Cl_2F_6NO$	1.6
244,246	$C_5H_5ClF_6NO$	6.2
216,218	C_3HClF_6NO	8.2
158,160,162,164	$C_4H_5Cl_3$	37.2
123,125,127	$C_4H_5Cl_2$	22.1
111,113,115	$C_3H_5Cl_2$	25.5
69	CF_3	33.5
49,51	CH_2Cl	8.5
43	C_2H_3O	100.0

1-NN-Bistrifluoromethylamino-3-(NN-bistrifluoromethylamino-oxy)-2-methyl-2,3,3-trichloropropane (M, 478,480,482,484)

$(CF_3)_2NCH_2CMeClCCl_2ON(CF_3)_2$ (30) $C_8H_5Cl_3F_{12}N_2O$

m/e	Assignment (R^+)	% Int. base
277,279,281	$C_5H_3Cl_2F_6NO$	14.4
275,277,279	$C_6H_5Cl_2F_6N$	0.1
260,262	$C_5H_2Cl_2F_6N$	0.5
228,230	$C_5H_5ClF_6N$	6.1
182	$C_3H_2F_6NO$	12.9
166	$C_3H_2F_6N$	100.0
158,160,162,164	$C_4H_5Cl_3$	5.4
144,146,148,150	$C_3H_3Cl_3$	3.1
133	C_2F_5N	5.6
123,125,127	$C_4H_5Cl_2$	2.6
111,113,115	$C_3H_5Cl_2$	5.7
99	-	12.4
97	-	24.4
95	-	14.8
90,92	C_3H_3OCl	17.4
78	$C_2H_2F_2N$	28.8
69	CF_3	54.8
43	C_2H_3O	8.3
41	C_3H_5	4.8
39	C_3H_3	7.1

1-(NN-Bistrifluoromethylamino-oxy)-2-methyl-1,1,2,3-tetrachloropropane $(CF_3)_2NOCCl_2CMeClCH_2Cl$ (31) $C_6H_5Cl_4F_6NO$ (tentatively identified) (M, 361,363,365,367)

m/e	Assignment (R^+)	% Int. base
326,328,330,332	$C_6H_5Cl_3F_6NO$	100.0
312,314	$C_5H_3Cl_3F_6NO$	2.2
290,292,294	$C_6H_4Cl_2F_6NO$	25.9
250,252	$C_3Cl_2F_6NO$	2.1
216,218	C_3HClF_6NO	8.0
193,195,197,199	$C_4H_5Cl_4$	39.4
158,160,162	$C_4H_5Cl_3$	29.2
157,159,161	$C_4H_4Cl_3$	50.3
150	C_2HF_5NO	5.7
144,146,148,150	$C_3H_3Cl_3$	25.5
123,125	$C_4H_5Cl_2$	18.6
111,113,115	$C_3H_5Cl_2$	77.1
69	CF_3	37.9
49,51	CH_2Cl	17.6
41	C_3H_5	9.3
39	C_3H_3	22.2

1-(NN-Bistrifluoromethylamino-oxy)-2-methyl-2-phenylpropane

$(CF_3)_2NOCH_2CMe_2Ph$ (39) $C_{12}H_{13}F_6NO$ (M, 301)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
301	M	1.0	91	C_7H_7	13.1
169	C_2HF_6NO	6.5	88	CF_4	17.4
150	C_2HF_5NO	6.0	81	C_5H_5O	12.7
149	$C_{10}H_{13}O$	0.7	77	C_6H_5	1.3
133	$C_2F_5N/C_{10}H_{13}$	2.8	69	CF_3	100.0
119	C_9H_{11}	20.7	58	C_3H_6O	14.6
118	C_9H_{10}	1.2	31	CF	11.4
117	C_9H_9	1.0			

NN-Bistrifluoromethylaminochlorobenzene $(CF_3)_2NC_6H_4Cl$ (52)

$C_8H_4ClF_6N$ (M, 263, 265)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
263,265	M	75.5	77	C_6H_5/C_3H_4Cl	17.2
244,246	$C_8H_4ClF_5N$	16.2	75	C_6H_3/C_3H_4Cl	15.5
228	$C_8H_4F_6N$	0.1	69	CF_3	100.0
194,196	$C_7H_4ClF_3N$	29.4	63	C_5H_3	12.6
175,177	$C_7H_4ClF_2N$	29.9	51	C_4H_3	12.2
159	$C_7H_4F_3N$	23.6	50	C_4H_2	20.0
112,114	C_6H_5Cl	38.2	39	C_3H_3	7.1
111,113	C_6H_4Cl	14.7	28	C_2H_4	33.3
99,101	C_5H_4Cl	7.5			

NN-bistrifluoromethylamino-t-butylbenzene

$(CF_3)_2NC_6H_4CMe_3$ $C_{12}H_{13}F_6N$ (M, 285)

m/e	Assignment (R^+)	% Int. base	
		3-isomer (41)	4-isomer (40)
285	M	35.2	24.1
270	$C_{11}H_{10}F_6N$	100.0	100.0
266	$C_{12}H_{13}F_5N$	11.9	9.5
242	$C_9H_6F_6N$	59.5	50.7
133	$C_2F_5N/C_{10}H_{13}$	5.1	2.9
118	C_9H_{10}	1.5	0.7
117	C_9H_9	4.4	3.2
116	C_9H_8	2.9	2.0
115	C_9H_7	6.6	4.6
109	C_7H_6F	7.0	3.4
91	C_7H_7	7.4	5.0
77	C_6H_5	7.3	5.6
69	CF_3	13.0	9.6
57	C_4H_9	4.2	4.4
41	C_3H_5	58.1	54.4
39	C_3H_3	10.2	7.1
28	C_2H_4	73.2	74.3

Bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)-t-butylcyclohexene $C_{18}H_{14}F_{24}N_4O_2$ (M, 774)

m/e	Assignment (R^+)	% Int. base
622	$C_{16}H_{14}F_{18}N_3O_2$	0.4
607	$C_{15}H_{11}F_{18}N_3O_2$	0.3
606	$C_{15}H_{10}F_{18}N_3O_2/C_{16}H_{14}F_{18}N_3O$	2.1
454	$C_{14}H_{14}F_{12}N_2O$	6.3
453	$C_{14}H_{13}F_{12}N_2O$	1.0
439	$C_{13}H_{11}F_{12}N_2O$	1.6
438	$C_{13}H_{10}F_{12}N_2O/C_{14}H_{14}F_{12}N_2$	7.6
437	$C_{14}H_{13}F_{12}N_2$	1.0
423	$C_{13}H_{11}F_{12}N_2$	6.4
318	$C_{12}H_{14}F_6NO_2$	2.9
302	$C_{12}H_{14}F_6NO$	2.0
286	$C_{12}H_{14}F_6N$	5.5
285	$C_{12}H_{13}F_6N$	2.4
270	$C_{11}H_{10}F_6N$	6.7
166	$C_3H_2F_6N$	24.6
134	$C_{10}H_{14}$	2.8
133	$C_{10}H_{13}/C_2F_5N$	4.3
69	CF_3	55.9
57	C_4H_9	100.0
41	C_3H_5	26.0
28	C_2H_4	69.4

Mixture of bis(NN-bistrifluoromethylamino)-bis(NN-bistrifluoromethylamino-oxy)chlorocyclohexene (57) $C_{14}H_5ClF_{24}N_4O_2$ (M, 752,754) and NN-bistrifluoromethylaminochlorobenzene $C_8H_4ClF_6N$ (M, 263,265) (tentatively identified)

m/e	Assignment (R^+)	% Int. base
600	$C_{12}H_5ClF_{18}N_3O_2$	0.1
584,586	$C_{12}H_5ClF_{18}N_3O$	2.1
432,434	$C_{10}H_5ClF_{12}N_2O$	3.9
416,418	$C_{10}H_5ClF_{12}N_2$	24.9
397	$C_{10}H_5F_{12}N_2O$	2.6
381	$C_{10}H_5F_{12}N_2$	1.6
296,298	$C_8H_5ClF_6NO_2$	1.0
280,282	$C_8H_5ClF_6NO$	11.2
279,281	$C_8H_4ClF_6NO$	4.8
264,266	$C_8H_5ClF_6N$	10.1
263,265	$C_8H_4ClF_6N$	3.9
244,246	$C_8H_4ClF_5N$	7.9
194,196	$C_7H_4ClF_3N$	4.0
166	$C_3H_2F_6N$	14.8
150	C_2HF_5NO	11.9
133	C_2F_5N	3.9
112,114	C_6H_5Cl	15.0
111,113	C_6H_4Cl	5.5
69	CF_3	100.0

1,1-Dimethyl-2-(NN-bistrifluoromethylamino-oxy)-2-oxoethyl acetate $(CF_3)_2NOCOCMe_2OAc$ (59) $C_8H_9F_6NO_4$ (M, 297)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
282	$C_7H_6F_6NO_4$	0.1	69	CF_3	47.0
238	$C_6H_6F_6NO_2$	0.2	59	$C_2H_3O_2$	38.9
196	$C_3F_6NO_2$	0.2	58	$C_2H_2O_2$	14.5
145	$C_6H_2O_4$	2.9	44	CO_2	57.7
133	C_2F_5N	4.6	43	C_2H_3O	100.0
129	$C_6H_9O_3$	7.9	42	C_2H_2O	14.1
114	$C_5H_6O_3/C_2F_4N$	3.3	41	C_3H_5	16.1
101	$C_5H_9O_2$	35.0			

NN-Bistrifluoromethylamino-oxycyclopropane carboxylate $\overline{CH_2CH_2}CHCOON(CF_3)_2$ (64) $C_6H_5F_6NO_2$ (M, 237)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
218	$C_6H_5F_5NO_2$	0.1	68	C_4H_4O	1.3
169	C_2HF_6NO	0.1	55	C_3H_3O	2.2
166	$C_3H_2F_6N$	0.2	44	CO_2	3.3
150	C_2HF_5NO	0.2	41	C_3H_5/C_2HO	51.8
133	C_2F_5N	0.5	40	C_3H_4	7.4
85	$C_4H_5O_2$	0.1	39	C_3H_3	31.5
69	CF_3/C_4H_5O	100.0	29	C_2H_5/CHO	5.4

ca. 2.6:1 Mixture of 1,1-dimethyl-2-(NN-bistrifluoromethylamino-oxy)ethyl acetate $(CF_3)_2NOCH_2CMe_2OAc$ (60) $C_8H_{11}F_6NO_3$ (M, 283) and 1,1-dimethyl-2,2-bis(NN-bistrifluoromethylamino-oxy)ethyl acetate $\left[(CF_3)_2NO\right]_2CHCMe_2OAc$ (61) $C_{10}H_{10}F_{12}N_2O_4$ (M, 405) (tentatively identified).

m/e	Assignment (R^+)	% Int. base
268	$C_7H_8F_6NO_3$	2.4
224	$C_6H_8F_6NO$	11.1
223	$C_6H_7F_6NO$	25.9
115	$C_6H_{11}O_2$	4.7
114	$C_2F_4N/C_6H_{10}O_2$	13.3
111	$C_6H_7O_2$	19.7
101	$C_5H_9O_2$	33.6
69	CF_3	71.0
59	$C_2H_3O_2$	23.4
56	C_4H_8	34.4
55	C_4H_7	68.9
44	CO_2	50.6
43	C_2H_3O/C_3H_7	100.0
42	C_2H_2O/C_3H_6	29.9
41	C_3H_5	54.3
39	C_3H_3	40.9
29	C_2H_5/CHO	52.7
28	C_2H_4/CO	37.6

Cyclopropyl-(NN-bistrifluoromethylamino-oxy)phenylmethane

$CH_2CH_2CHCHPhON(CF_3)_2$ (69) $C_{12}H_{11}F_6NO$ (M, 299)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
298	$C_{12}H_{10}F_6NO$	0.3	105	C_8H_9/C_7H_5O	10.2
257	$C_9H_5F_6NO$	0.4	91	C_7H_7	50.9
131	$C_{10}H_{11}$	100.0	77	C_6H_5	15.4
130	$C_{10}H_{10}$	7.3	69	CF_3	11.3
129	$C_{10}H_9$	13.0	51	C_4H_3	10.9
128	$C_{10}H_8$	7.8	44	C_2H_4O	5.4
116	C_9H_8	12.6	41	C_3H_5	5.2
115	C_9H_7	11.4	39	C_3H_3	8.4

1-(NN-Bistrifluoromethylamino)methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene

$(CF_3)_2NCH_2C{:}CHCH_2CH[CMe_2ON(CF_3)_2]CH_2CH_2$ (82) $C_{14}H_{16}F_{12}N_2O$ (M, 456)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
288	$C_{12}H_{16}F_6N$	19.1	93	-	51.4
287	$C_{12}H_{15}F_6N$	15.5	91	-	36.1
246	$C_9H_{10}F_6N$	4.1	79	C_6H_7	66.6
243	$C_9H_{10}F_5NO$	10.3	78	$C_6H_6/C_2H_2F_2N$	27.6
232	-	53.7	69	CF_3	80.2
210	$C_5H_6F_6NO$	22.4	58	C_3H_6O	33.5
166	$C_3H_2F_6N$	100.0	43	C_3H_7/C_2H_3O	93.1
136	$C_{10}H_{16}$	4.8	41	C_3H_5	34.1
135	$C_{10}H_{15}$	23.1			
121	C_9H_{13}	35.6			

10-(NN-Bistrifluoromethylamino-oxy)-2-pinene

$(CF_3)_2NOCH_2C{:}CHCH_2CHCH_2CHCMe_2$ $C_{12}H_{15}F_6NO$ (72) (M, 303)

m/e	Assignment (R^+)	% Int. base
303	M	3.3
288	$C_{11}H_{12}F_6NO$	0.4
182	$C_3H_2F_6NO$	1.0
135	$C_{10}H_{15}$	37.1
119	C_9H_{11}	10.8
107	C_7H_7O	44.6
105	C_8H_9	13.7
93	C_7H_9	69.4
92	C_7H_8	21.7
91	C_7H_7	100.0
81	C_6H_9/C_5H_5O	17.0
79	C_6H_7	88.2
78	C_6H_6	11.3
77	C_6H_5	68.9
69	CF_3	43.5
67	C_5H_7	12.3
55	C_4H_7	25.8
53	C_3H_3O	15.8
43	C_2H_3O/C_3H_7	46.0
41	C_3H_5	52.5
39	C_3H_3	18.8

1-(NN-Bistrifluoromethylamino-oxy)methyl-4-[2'-(NN-bistrifluoromethylamino-oxy)propyl]cyclohex-1-ene $C_{14}H_{16}F_{12}N_2O_2$

$(CF_3)_2NOCH_2\overset{\Gamma}{C}:CHCH_2CH\left[CMe_2ON(CF_3)_2\right]\overset{\lrcorner}{C}H_2CH_2$ (73) (M, 472)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
471	$C_{14}H_{15}F_{12}N_2O_2$	0.1	107	C_8H_{11}	14.0
304	$C_{12}H_{16}F_6NO$	0.7	105	C_8H_9/C_7H_7O	14.3
303	$C_{12}H_{15}F_6NO$	1.2	93	C_7H_9	15.2
302	$C_{12}H_{14}F_6NO$	7.8	92	C_7H_8	13.5
290	$C_{11}H_{14}F_6NO$	1.9	91	C_7H_7	53.8
262	$C_9H_{10}F_6NO$	1.1	81	C_6H_7	14.2
210	$C_5H_6F_6NO$	8.4	79	C_6H_5	17.0
182	$C_3H_2F_6NO$	0.2	69	CF_3	100.0
150	C_2HF_5NO	15.4	58	C_3H_6O	2.9
136	$C_{10}H_{16}$	2.6	55	C_3H_3O/C_4H_7	12.3
135	$C_{10}H_{15}$	11.0	43	C_3H_7/C_2H_3O	79.5
134	$C_{10}H_{14}$	19.9	41	C_3H_5	25.9
133	$C_{10}H_{13}/C_2F_5N$	14.6	39	C_3H_3	13.6
119	C_2F_5	25.0			

2(10)-Bis(NN-bistrifluoromethylamino-oxy)pinane (M, 472)

$(CF_3)_2NOCH_2CON(CF_3)_2CH_2CH_2CHCH_2CHCMe_2$ (74) $C_{14}H_{16}F_{12}N_2O_2$

m/e	Assignment (R^+)	% Int. base	
		Diastereo-isomer (1)	Diastereo-isomer (2)
472	M	0.1	-
471	$C_{14}H_{15}F_{12}N_2O_2$	1.5	0.5
417	$C_{10}H_8F_{12}N_2O_2$	1.3	1.2
320	$C_{12}H_{16}F_6NO_2$	0.9	0.3
304	$C_{12}H_{16}F_6NO$	23.0	21.9
290	$C_{11}H_{14}F_6NO$	5.7	5.3
248	$C_8H_8F_6NO$	27.2	21.7
182	$C_3H_2F_6NO$	1.5	1.2
136	$C_{10}H_{16}$	35.9	30.8
135	$C_{10}H_{15}$	32.5	31.4
95	C_7H_{11}/C_6H_7O	39.0	17.1
93	C_7H_9	26.3	24.4
83	C_6H_{11}/C_5H_7O	22.6	21.4
81	C_6H_9/C_5H_5O	18.2	16.0
80	C_6H_8	23.4	18.1
79	C_6H_7	26.4	19.9
69	CF_3	100.0	100.0
67	C_5H_7/C_4H_3O	22.0	19.3
55	C_4H_7	28.6	27.0
43	C_3H_7/C_2H_3O	53.8	42.1
41	C_3H_5	40.6	39.7

3-(NN-Bistrifluoromethylamino-oxy)-2(10)-pinene *

$CH_2{:}\overline{CCHON(CF_3)_2CH_2}\overline{CHCH_2}\overline{CHCMe_2}$ (78) $C_{12}H_{15}F_6NO$ (M, 303)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
135	$C_{10}H_{15}$	37.1	69	CF_3	100.0
107	C_8H_{11}/C_7H_7O	33.1	57	C_3H_5O	20.1
93	C_7H_9/C_6H_5O	92.4	55	C_3H_3O/C_4H_7	19.9
92	C_7H_8	17.8	53	C_4H_5	20.1
91	C_7H_7	49.0	43	C_2H_3O/C_3H_7	60.1
81	C_6H_9	17.3	41	C_3H_5	90.7
79	C_6H_7	72.1	39	C_3H_3	28.4
77	C_6H_5	34.8	29	C_2H_5/CHO	15.0

2,3-Bis(NN-bistrifluoromethylamino-oxy)pinane * (M, 472)

$CH_3\overline{CON(CF_3)_2CHON(CF_3)_2CH_2}\overline{CHCH_2}\overline{CHCMe_2}$ (79) $C_{14}H_{16}F_{12}N_2O_2$

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
304	$C_{12}H_{16}F_6NO$	4.4	83	C_5H_7O	38.7
250	$C_8H_{10}F_6NO$	30.7	82	C_5H_6O	13.0
136	$C_{10}H_{16}$	34.5	81	C_6H_9/C_5H_5O	13.1
135	$C_{10}H_{15}$	38.0	80	C_6H_8	19.5
109	C_7H_9O	10.8	69	CF_3	100.0
107	C_8H_{11}	14.5	55	C_4H_7/C_2H_3O	22.5
93	C_7H_9/C_6H_5O	97.6	43	C_2H_3O/C_3H_7	91.4
91	C_7H_7	11.9	41	C_3H_5	32.3

* Mixture of diastereoisomers.

A mixture of 10-NN-bistrifluoromethylamino-2-pinene $(CF_3)_2NCH_2C{:}CHCH_2CHCH_2CHCMe_2$ (81) $C_{12}H_{15}F_6N$ ($\underline{M}_1$, 287) and 10-(NN-bistrifluoromethylamino-oxy)-2-pinene $(CF_3)_2NOCH_2C{:}CHCH_2CHCH_2CHCMe_2$ (72) $C_{12}H_{15}F_6NO$ ($\underline{M}_2$, 303).

m/e	Assignment (R^+)	% Int. base
303	$\underline{M}_2$	0.2
288	$C_{11}H_{12}F_6NO$	0.5
287	$\underline{M}_1$	2.8
272	$C_{11}H_{12}F_6N$	2.8
243	$C_9H_{10}F_5NO$	23.2
166	$C_3H_2F_6N$	100.0
135	$C_{10}H_{15}$	10.1
107	C_7H_7O	18.4
105	C_7H_5O	17.7
93	C_6H_5O	49.5
91	C_7H_7	90.2
79	C_6H_7	67.0
78	C_6H_6	49.8
69	CF_3	48.9
43	C_3H_7/C_2H_3O	48.3
41	C_3H_5	59.2
39	C_3H_3	35.5
28	C_2H_4	42.0

1-(NN-Bistrifluoromethylamino)methyl-4-isopropylcyclohex-1-ene $(CF_3)_2NCH_2\overline{C:CHCH_2CH(CHMe_2)CH_2CH_2}$ (83) $C_{12}H_{17}F_6N$ (M,289)

m/e	Assignment (R^+)	% Int. base
289	M	14.0
274	$C_{11}H_{14}F_6N$	2.5
246	$C_9H_{10}F_6N$	5.4
166	$C_3H_2F_6N$	90.7
137	$C_{10}H_{17}$	12.6
136	$C_{10}H_{16}$	18.4
123	C_9H_{15}	81.7
121	C_9H_{13}	21.6
95	C_7H_{11}/C_6H_7O	21.9
93	C_7H_9/C_6H_5O	99.8
91	C_7H_7	38.6
81	C_6H_9/C_5H_5O	68.2
79	C_6H_7	75.2
78	$C_6H_6/C_2H_2F_2N$	38.6
77	C_6H_5	33.7
69	CF_3	95.5
68	C_5H_8	32.9
67	C_5H_7	100.0
55	C_4H_7	48.0
53	C_4H_5	21.4
43	C_3H_7/C_2H_3O	49.0
41	C_3H_5	64.9

2-Exo-3-exo-bis(NN-bistrifluoromethylamino-oxy)norborn-5-ene (C) (90), and the corresponding 2-exo-3-endo-isomer (B) (89)

$(CF_3)_2NOCHCHON(CF_3)_2CHCH:CHCHCH_2$ $C_{11}H_8F_{12}N_2O_2$ (M, 428)

m/e	Assignment (R^+)	% Int. base (C)	(B)
427	$C_{11}H_7F_{12}N_2O_2$	0.1	-
402	$C_9H_6F_{12}N_2O_2$	0.9	-
260	$C_9H_8F_6NO$	4.2	1.0
182	$C_3H_2F_6NO$	2.8	0.1
166	$C_3H_2F_6N$	3.9	0.3
150	C_2HF_5NO	5.9	0.2
108	C_7H_8O	24.7	12.4
107	C_7H_7O	7.3	3.6
92	C_7H_8	9.7	2.6
91	C_7H_7	14.5	3.4
80	C_5H_4O	10.7	5.7
79	C_6H_7	48.5	14.4
78	C_6H_6	5.2	1.1
77	C_6H_5	30.6	6.6
69	CF_3	27.1	6.3
66	C_5H_6	100.0	100.0
65	C_5H_5	7.7	4.4
55	C_3H_3O	5.7	0.4
41	C_3H_5	9.9	3.0
39	C_3H_3	9.8	4.4
28	C_2H_4	30.6	4.8

Isomers (D and E) of 2-exo-6-bis(NN-bistrifluoromethylamino-oxy)nortricyclane $(CF_3)_2NOCHCHCHCHCHON(CF_3)_2CHCH_2$ (91) and (92) $C_{11}H_8F_{12}N_2O_2$ (M, 428)

m/e	Assignment (R^+)	% Int. base (D)	% Int. base (E)
260	$C_9H_8F_6NO$	35.1	33.5
166	$C_3H_2F_6N$	7.8	6.6
150	C_2HF_5NO	3.6	2.7
110	-	12.6	0.4
108	C_7H_8O	50.0	83.8
107	C_7H_7O	14.4	17.2
93	C_6H_5O	8.5	2.2
92	C_7H_8	16.2	20.5
91	C_7H_7	32.5	29.1
81	C_5H_5O	11.5	8.1
80	C_5H_4O	18.1	20.6
79	C_6H_7	100.0	100.0
78	C_6H_6	10.8	8.5
77	C_6H_5	55.1	43.7
69	CF_3	43.3	17.5
67	C_4H_3O	18.5	4.7
66	C_5H_6	92.6	28.5
41	C_3H_5	9.4	4.4
39	C_3H_3	12.9	10.9
28	C_2H_4	-	49.1

Mixture of isomers of 2-exo-3,5,6-tetrakis(NN-bistrifluoromethylamino-oxy)norbornane (93) (M, 764)

$(CF_3)_2NOCHCHON(CF_3)_2CHCHON(CF_3)_2CHON(CF_3)_2CHCH_2$ $C_{15}H_8F_{24}N_4O_4$

m/e	Assignment (R^+)	% Int. base*	m/e	Assignment (R^+)	% Int. base*
596	$C_{13}H_8F_{18}N_3O_3$	5.8	96	-	30.6
595	$C_{13}H_7F_{18}N_3O_3$	40.5	95	-	71.0
428	$C_{11}H_8F_{12}N_2O_2$	11.7	94	C_6H_6O	37.5
427	$C_{11}H_7F_{12}N_2O_2$	74.2	93	C_6H_5O	23.2
349	-	22.3	92	C_7H_8	21.5
276	$C_9H_8F_6NO_2$	19.0	82	C_5H_6O	49.5
275	$C_9H_7F_6NO_2$	18.6	81	C_5H_5O	61.7
260	$C_9H_8F_6NO$	33.5	80	C_5H_4O	29.1
259	$C_9H_7F_6NO$	65.6	79	C_6H_7	83.6
247	$C_8H_7F_6NO$	11.0	78	C_6H_6	30.9
246	$C_8H_6F_6NO$	28.4	69	CF_3	100.0
234	$C_7H_6F_6NO$	13.4	67	C_5H_7	62.8
150	C_2HF_5NO	15.3	66	C_5H_6	52.1
124	$C_7H_8O_2$	43.4	55	C_3H_3O	49.5
123	$C_7H_7O_2$	69.7	41	C_3H_5	29.4
108	C_7H_8O	46.0	28	C_2H_4	73.2
107	C_7H_7O	80.3			

* Figures quoted for isomer (F); the other isomers (G-I) gave similar results.

3-(NN-Bistrifluoromethylamino-oxy)cyclo-octa-1,5-diene

$(CF_3)_2NO\overline{CHCH:CHCH_2CH_2CH:CHCH_2}$ (99) $C_{10}H_{11}F_6NO$ (M, 275)

m/e	Assignment (R^+)	% Int. base
275	M	1.7
274	$C_{10}H_{10}F_6NO$	0.7
234	$C_7H_6F_6NO$	1.3
221	$C_6H_5F_6NO$	77.1
107	C_8H_{11}	100.0
105	C_8H_9	13.5
91	C_7H_7	42.6
81	C_6H_9	14.0
80	C_6H_8	18.4
79	C_6H_7	94.3
78	C_6H_6	17.3
77	C_6H_5	28.9
69	CF_3	67.2
68	C_5H_8	25.7
67	C_5H_7	25.4
55	C_4H_7/C_3H_3O	18.4
54	C_4H_6/C_3H_2O	29.8
53	C_4H_5	24.6
41	C_3H_5	93.2
40	C_3H_4	16.4
39	C_3H_3	59.5

A mixture of components (A and B) tentatively identified as bis(NN-bistrifluoromethylamino-oxy)cyclo-octene $C_{12}H_{12}F_{12}N_2O_2$ (M, 444) and bis(NN-bistrifluoromethylamino-oxy)cyclo-octadiene $C_{12}H_{10}F_{12}N_2O_2$ (M, 442)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
416	$C_{10}H_8F_{12}N_2O_2$	0.4	91	C_7H_7	34.1
290	$C_{10}F_{10}F_6NO_2$	0.7	82	C_6H_{10}	11.6
276	$C_{10}H_{12}F_6NO$	1.4	81	C_6H_9	42.0
275	$C_{10}H_{11}F_6NO$	0.4	80	C_6H_8	41.2
274	$C_{10}H_{10}F_6NO$	3.8	79	C_6H_7	100.0
248	$C_8H_8F_6NO$	22.5	78	C_6H_6	30.4
150	$C\ HF_5NO$	9.4	77	C_6H_5	21.5
124	$C_8H_{12}O$	20.5	69	CF_3	70.0
122	$C_8H_{10}O$	13.3	68	C_5H_8/C_4H_4O	18.5
108	C_8H_{12}	11.0	67	C_5H_7	39.8
107	C_8H_{11}	53.2	55	C_4H_7/C_3H_3O	32.2
106	C_8H_{10}	51.1	53	C_4H_5	17.3
105	C_8H_9	27.9	41	C_3H_5	45.3
95	C_7H_{11}	25.4	39	C_3H_3	27.9
93	C_7H_9	20.8	28	C_2H_4	92.4

A mixture of components (C and D) tentatively identified as bis(NN-bistrifluoromethylamino-oxy)cyclo-octene $C_{12}H_{12}F_{12}N_2O_2$ (M, 444) and bis(NN-bistrifluoromethylamino-oxy)cyclo-octadiene $C_{12}H_{10}F_{12}N_2O_2$ (M, 442)

m/e	Assignment (R^+)	% Int. base
425	$C_{12}H_{12}F_{11}N_2O_2$	0.4
292	$C_{10}H_{12}F_6NO_2$	0.5
290	$C_{10}H_{10}F_6NO_2$	0.2
276	$C_{10}H_{12}F_6NO$	0.4
274	$C_{10}H_{10}F_6NO$	0.8
166	$C_3H_2F_6N$	5.3
150	C_2HF_5NO	3.7
133	C_2F_5N	8.7
124	$C_8H_{12}O$	1.1
122	$C_8H_{10}O$	1.8
81	C_6H_9	9.6
79	C_6H_7	8.6
69	CF_3	100.0
67	C_5H_7/C_4H_3O	6.9
57	C_4H_9/C_3H_5O	7.3
55	C_4H_7	10.2
44	C_2H_4O	19.1
43	C_2H_3O/C_3H_7	7.1
41	C_3H_5	10.5
39	C_3H_3	7.9

1-NN-Bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)cyclo-oct-5-ene $(CF_3)_2NCHCH_2CH_2CH{:}CHCH_2CH_2CHON(CF_3)_2$

(103) $C_{12}H_{12}F_{12}N_2O$ (M, 428)

m/e	Assignment (R^+)	% Int. base	
		Diastereo-isomer (1)	Diastereo-isomer (2)
400	$C_{10}H_8F_{12}N_2O$	4.8	-
276	$C_{10}H_{12}F_6NO$	3.6	2.3
260	$C_{10}H_{12}F_6N$	7.7	15.9
218	$C_7H_6F_6N$	10.0	12.1
192	$C_5H_4F_6N$	40.6	36.3
166	$C_3H_2F_6N$	32.3	25.2
124	$C_8H_{12}O$	6.9	7.1
108	C_8H_{12}	6.6	5.9
107	C_8H_{11}	52.3	49.8
95	C_7H_{11}	17.9	9.9
91	C_7H_7	12.5	11.8
81	C_5H_5O/C_6H_9	100.0	100.0
80	C_6H_8	18.6	13.1
79	C_6H_7	74.5	79.5
69	CF_3	48.1	49.3
67	C_5H_7	36.7	31.9
55	C_3H_3O/C_4H_7	19.8	18.7
53	C_4H_5	15.0	14.0
43	C_2H_3O/C_3H_7	10.9	9.1
41	C_3H_5	58.2	55.0
39	C_3H_3	15.5	15.3

3-(NN-Bistrifluoromethylamino-oxy)cyclo-oct-1-ene

$(CF_3)_2NO\overline{CHCH:CHCH_2CH_2CH_2CH_2CH_2}$ (105) $C_{10}H_{13}F_6NO$ (M, 277)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
277	M	0.2	79	C_6H_7	18.7
276	$C_{10}H_{12}F_6NO$	2.1	69	CF_3	22.9
150	C_2HF_5NO	6.9	67	C_5H_7	100.0
125	$C_8H_{13}O$	0.9	55	C_4H_7/C_3H_3O	59.6
124	$C_8H_{12}O$	2.7	53	C_4H_5	10.2
109	C_8H_{13}	54.7	43	C_3H_7/C_2H_3O	17.5
108	C_8H_{12}	5.3	41	C_3H_5	54.1
107	C_8H_{11}	9.2	39	C_3H_3	24.6
81	C_6H_9/C_5H_5O	26.7	29	C_2H_5/CHO	22.4

1,2-Bis(NN-bistrifluoromethylamino-oxy)cyclo-octane (M, 446)

$(CF_3)_2NO\overline{CHCH_2CH_2CH_2CH_2CH_2CH_2}CHON(CF_3)_2$ (106) $C_{12}H_{14}F_{12}N_2O_2$

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
278	$C_{10}H_{14}F_6NO$	1.5	81	C_6H_9	16.5
150	C_2HF_5NO	10.6	69	CF_3	30.9
126	$C_8H_{14}O$	5.4	67	C_5H_7	54.3
110	C_8H_{14}	9.2	55	C_4H_7/C_3H_3O	54.6
109	C_8H_{13}	100.0	43	C_3H_7/C_2H_3O	21.8
98	$C_6H_{10}O$	15.1	41	C_3H_5	35.0
83	C_6H_{11}/C_5H_7O	14.7	28	C_2H_4	10.6

3-(NN-Bistrifluoromethylamino-oxy)-3-phenylpropene $(CF_3)_2NOCHPhCH:CH_2$ (109) and 3-(NN-bistrifluoromethylamino-oxy)-1-phenylpropene $(CF_3)_2NOCH_2CH:CHPh$ (110)

$C_{11}H_9F_6NO$ (M, 285)

m/e	Assignment (R^+)	% Int. base (109)	% Int. base (110)
285	M	0.3	0.9
150	C_2HF_5NO	0.7	-
133	C_2F_5N/C_9H_9O	0.4	0.5
131	C_9H_7O	1.1	3.0
117	C_9H_9	100.0	100.0
116	C_9H_8	9.3	7.7
115	C_9H_7	30.9	30.9
103	C_8H_7	3.1	4.3
91	C_7H_7	16.3	14.5
77	C_6H_5	8.6	10.7
69	CF_3	20.3	10.0
51	C_3H_5O	6.6	8.8
44	-	6.2	3.0
39	C_3H_3	5.7	6.6

1,2,3-Tri(NN-bistrifluoromethylamino-oxy)-3-phenylpropane .

$(CF_3)_2NOCH_2CHON(CF_3)_2CHPhON(CF_3)_2$ (111) $C_{15}H_9F_{18}N_3O_3$ (M,621)

m/e	Assignment (R^+)	% Int. base	
		Diastereo-isomer (1)	Diastereo-isomer (2)
453	$C_{13}H_9F_{12}N_2O_2$	1.5	-
452	$C_{13}H_8F_{12}N_2O_2$	10.2	6.4
301	$C_{11}H_9F_6NO_2$	4.8	4.1
285	$C_{11}H_9F_6NO$	1.7	0.6
284	$C_{11}H_8F_6NO$	4.6	4.1
258	$C_9H_6F_6NO$	18.8	31.8
242	$C_9H_6F_6N$	2.5	1.7
182	$C_3H_2F_6NO$	2.0	1.0
150	C_2HF_5NO	3.9	1.2
133	C_2F_5N/C_9H_9O	11.2	12.0
132	C_9H_8O	19.1	19.9
119	-	29.8	31.0
117	C_9H_9	100.0	100.0
116	C_9H_8	7.3	8.5
106	C_7H_6O/C_7H_5N	22.6	29.3
105	$C_8H_9/C_7H_5O/C_7H_7N$	53.1	55.9
91	C_7H_7	78.2	80.2
77	C_6H_5	23.1	23.1
69	CF_3	88.4	68.5

1,2,5-Tri(NN-bistrifluoromethylamino-oxy)pent-3-ene (component G) $(CF_3)_2NOCH_2CHON(CF_3)_2CH{:}CHCH_2ON(CF_3)_2$ (115)
$C_{11}H_7F_{18}N_3O_3$ and unidentified component (F)

m/e	Assignment (R^+)	% Int. base (G)	(F)
552	$C_{11}H_7F_{17}N_3O_3$	1.2	1.3
403	$C_9H_7F_{12}N_2O_2$	13.5	11.9
234	$C_7H_6F_6NO$	6.6	8.3
221	$C_6H_5F_6NO$	2.3	2.4
208	$C_5H_4F_6NO$	10.6	9.4
192	$C_5H_7F_5NO$	17.0	15.6
182	$C_3H_2F_6NO$	7.5	14.1
166	$C_3H_2F_6N$	8.1	9.3
150	C_2HF_5NO	8.3	13.7
83	C_5H_7O	5.8	9.7
82	C_5H_6O	11.6	20.5
81	C_5H_5O	9.5	13.3
69	CF_3	100.0	100.0
68	C_4H_4O	9.6	14.8
67	C_5H_7	31.9	39.0
66	C_5H_6	54.4	25.7
55	C_3H_3O	24.7	31.7
41	C_3H_5	30.1	35.6
40	C_3H_4	19.8	6.1
39	C_3H_3	14.3	18.8
29	C_2H_5/CHO	27.0	18.8

3-(NN-Bistrifluoromethylamino-oxy)penta-1,4-diene (component C) $[CH_2:CH]_2CHON(CF_3)_2$ (116) and 1-(NN-bistrifluoromethylamino-oxy)penta-2,4-diene (component D) $(CF_3)_2NOCH_2CH:CHCH:CH_2$ (117) $C_7H_7F_6NO$ (M, 235)

m/e	Assignment (R^+)	% Int. base	
		3-isomer (116)	1-isomer (117)
235	M	0.5	2.5
150	C_2HF_5NO	1.3	2.5
81	C_5H_5O	2.4	2.8
69	CF_3	42.6	39.1
68	C_4H_4O	5.8	4.6
67	C_5H_7	100.0	100.0
66	C_5H_6	4.1	3.8
65	C_5H_5	10.8	7.5
55	C_3H_3O	7.2	3.8
54	C_3H_2O	5.5	1.5
53	C_4H_5	9.1	6.3
52	C_4H_4	3.1	2.5
51	C_4H_3	5.4	4.0
50	CF_2/C_4H_2	5.6	3.5
41	C_3H_5	32.8	29.8
40	C_3H_4	3.1	10.6
39	C_3H_3	17.9	16.1
28	C_2H_4	41.7	-

4,5-Bis(NN-bistrifluoromethylamino-oxy)pent-1-ene

$(CF_3)_2NOCH_2CHON(CF_3)_2CH_2CH{:}CH_2$ (118) $C_9H_8F_{12}N_2O_2$ (M, 404)
(tentatively identified)

m/e	Assignment (R^+)	% Int. base
403	$C_9H_7F_{12}N_2O_2$	5.7
363	$C_6H_3F_{12}N_2O_2$	0.3
234	$C_7H_6F_6NO$	2.2
218	$C_7H_6F_6N$	1.2
208	$C_5H_4F_6NO$	23.2
192	$C_5H_7F_5NO$	19.5
182	$C_3H_2F_6NO$	13.9
166	$C_3H_2F_6N$	14.5
94	$C_2H_2F_2NO$	10.1
92	-	11.3
82	C_5H_6O	11.7
69	CF_3	100.0
68	C_5H_8/C_4H_4O	5.4
67	C_5H_7	28.8
55	C_4H_7/C_3H_3O	39.0
54	C_4H_6/C_3H_2O	10.0
41	C_3H_5	34.9
39	C_3H_3	15.7
29	CHO	26.4

1-NN-Bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)-3-phenylpropane $(CF_3)_2NCH_2CH(CH_2Ph)ON(CF_3)_2$ (121)

$C_{13}H_{10}F_{12}N_2O$ (M, 438)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
438	M	2.5	104	C_8H_8	7.3
272	$C_{10}H_8F_6NO$	0.4	103	C_8H_7	2.0
271	$C_{10}H_7F_6NO$	1.2	91	C_7H_7	100.0
270	$C_{11}H_{10}F_6N$	11.5	78	$C_2H_2F_2N$	13.6
269	$C_{11}H_9F_6N$	5.4	77	C_6H_5	2.3
166	$C_3H_2F_6N$	67.9	69	CF_3	16.8
118	C_9H_{10}	1.8	65	C_5H_5	8.5
117	C_9H_9	10.4	28	C_2H_4	92.9

1-NN-Bistrifluoromethylamino-2-(NN-bistrifluoromethylamino-oxy)pent-4-ene $(CF_3)_2NCH_2CHON(CF_3)_2CH_2CH:CH_2$ (122)

$C_9H_8F_{12}N_2O$ (M, 388)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
346	$C_6H_2F_{12}N_2O$	5.6	68	C_5H_8	1.6
220	$C_7H_8F_6N$	18.3	67	C_5H_7	17.4
219	$C_7H_7F_6N$	5.8	54	C_4H_6	6.8
218	$C_7H_6F_6N$	2.5	53	C_4H_5	3.9
179	$C_4H_3F_6N$	10.8	43	C_2H_3O/C_3H_7	5.9
166	$C_3H_2F_6N$	100.0	42	C_2H_2O/C_3H_6	19.0
78	$C_2H_2F_2N$	36.0	41	C_3H_5	55.6
69	CF_3	47.3	39	C_3H_3	18.0

Mixture of telomers of general formulae

$(CF_3)_2N\left[C_7H_8\right]_xON(CF_3)_2$ (where x= 1,2,3,...)

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
675	-	0.6	175	-	12.8
597	-	0.7	174	-	13.4
581	-	2.8	166	$C_2H_3F_6N$	72.4
580	$C_{25}H_{24}F_{12}N_2$	0.3	161	-	11.4
503	$C_{18}H_{15}F_{12}N_2O$	0.9	148	-	8.2
427	$C_{23}H_{23}F_6N$	1.2	127	-	10.5
412	$C_{11}H_8F_{12}N_2O$	0.8	114	-	7.9
411	$C_{11}H_7F_{12}N_2O$	4.2	111	-	6.9
396	$C_{11}H_8F_{12}N_2$	0.4	109	C_7H_9O	12.6
395	$C_{11}H_7F_{12}N_2$	0.9	108	C_7H_8O	13.7
350	-	6.0	107	C_7H_7O	13.7
336	$C_{16}H_{16}F_6N$	0.4	96	-	8.9
327	-	19.2	92	C_7H_8	13.7
275	$C_{21}H_{23}$	0.9	91	C_7H_7	50.4
260	$C_9H_8F_6NO$	2.4	79	C_6H_7	52.7
259	$C_9H_7F_6NO$	2.5	78	C_6H_6	30.3
249	$C_{15}H_{16\ 2}N$	10.5	77	C_6H_5	37.9
244	$C_9H_8F_6N$	22.1	69	CF_3	100.0
243	$C_9H_7F_6N$	6.0	67	C_5H_7/C_4H_3O	10.1
192	-	26.5	66	C_5H_6	21.1
184	$C_{14}H_{16}$	1.4	65	C_5H_5	21.4

Mixture of NN-bistrifluoromethylamino-NN-bistrifluoromethylamino-oxy-substituted dimers of penta-1,4-diene

m/e	Assignment (R^+)	% Int. base	m/e	Assignment (R^+)	% Int. base
288	$C_{12}H_{16}F_6N$	4.9	93	C_7H_9	33.2
287	$C_{12}H_{15}F_6N$	3.2	91	C_7H_7	33.7
247	$C_9H_{11}F_6N$	0.2	85	C_5H_9O	11.8
246	$C_7H_{10}F_6N$	2.2	81	C_6H_9	15.3
182	$C_3H_2F_6NO$	2.7	80	C_6H_8	10.4
166	$C_3H_2F_6N$	48.3	79	C_6H_7	41.5
150	C_2HF_5NO	2.3	78	C_6H_6	26.2
136	$C_{10}H_{16}$	1.9	77	C_6H_5	7.7
135	$C_{10}H_{15}$	6.9	69	CF_3	100.0
134	$C_{10}H_{14}$	6.2	68	C_5H_8	3.1
133	C_2F_5N	8.4	67	C_5H_7	23.7
130	$C_9H_6O/C_{10}H_{10}$	14.8	44	C_2H_4O	96.1
121	C_9H_{13}	48.8	43	C_2H_3O/C_3H_7	12.8
119	C_9H_{11}	13.1	41	C_3H_5	22.0
111	$C_7H_{11}O$	10.5	39	C_3H_3	15.9
95	C_7H_{11}	10.6			

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